Monitoring of priority pollutants in dynamic stormwater discharges from urban areas

Birch, Heidi

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Heidi Birch

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Address: DTU Environment
Department of Environmental Engineering
Technical University of Denmark
Miljoevej, building 113
DK-2800 Kgs. Lyngby
Denmark

Phone reception: +45 4525 1600
Phone library: +45 4525 1610
Fax: +45 4593 2850

Homepage: http://www.env.dtu.dk
E-mail: reception@env.dtu.dk

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Preface

This thesis presents the outcome of a PhD project carried out at the Department of Environmental Engineering (DTU Environment), Technical University of Denmark (DTU) in the period from January 2008 to June 2012. The project was supervised by Associate Professor Peter Steen Mikkelsen and Associate Professor Hans-Christian Holten Lützhøft.

The thesis is based on five scientific papers. In the thesis, these papers are referred to with the roman numbers (e.g. **Paper I**).

I. **Birch, H.**, Mikkelsen, P.S., Jensen, J.K., Lützhøft, H.-C.H. (2011). Micropollutants in stormwater run-off and combined sewer overflow in the Copenhagen area, Denmark, *Water Science and Technology*, **64** (2), 485-493. DOI: 10.2166/wst.2011.687.

II. **Birch, H.**, Gouliarmou, V., Lützhøft, H.-C.H., Mikkelsen, P.S. and Mayer, P. (2010). Passive Dosing to determine the speciation of hydrophobic organic chemicals in aqueous samples, *Analytical Chemistry*, **82** (3), 1142-1146. DOI: 10.1021/ac902378w.

III. **Birch, H.,** Mayer, P., Lützhøft, H-C.H. and Mikkelsen, P.S. (in revision) Partitioning of fluoranthene between free and bound forms in stormwater runoff and urban waste waters using passive dosing.

IV. **Birch, H.,** Sharma, A.K., Vezzaro, L., Lützhøft, H.-C.H. and Mikkelsen, P.S. (manuscript). Velocity dependant sampling of micropollutants in stormwater using a flow-through passive sampler.

V. **Birch, H.,** Vezzaro, L. and Mikkelsen, P.S. (accepted) Model based monitoring of stormwater runoff quality. *In proceedings of the 9th international conference on Urban Drainage Modelling, Belgrade, 2012.*

The papers are included in the printed version of the thesis but not in the www version. Copies of the papers can be obtained from the Library at DTU Environment.

Department of Environmental Engineering
Technical University of Denmark
Miljoevej, Building 113
DK-2800 Kgs. Lyngby, Denmark
(library@env.dtu.dk)

The following articles and reports were prepared during the PhD project but they are not included as part of the thesis:

Birch, H., Mikkelsen, P.S., Jensen, J.K. and Lützhøft, H.-C.H. (2010). Xenobiotics in Stormwater Run-off and Combined Sewer Overflow. *Proc. 14th Int. Conf. on Diffuse Pollution and Eutrophication – DIPCON 2010, September 12-17, Baupré, Quebec, Canada*, Abstract (S901-IWA-4679R1, p. 124) and Full paper (S901, p. 247-252).

Birch, H., Sharma, A.K., Vezzaro, L., Mikkelsen, P.S. and Lützhøft, H.-C.H. (2011). Passive sampling and modeling of PAHs and heavy metals in stormwater runoff, *In Proceedings of the12th International Conference on Urban Drainage, Porto Alegre/Brazil, 11-16 September 2011*. Full paper PAP005248. 8 p.

Birch, H., Lützhøft, H.C.H. and Mikkelsen, P.S. (2010). Tungmetaller og miljøfremmede organiske stoffer i regnbetingede udledninger: nye stikprøvemålinger (Heavy metals and xenobiotics in stormwater discharges: new spot sample measurements), *danskVAND (Danish Water),* **78** (5), 37-40.

Fryd, O., Backhaus, A., Jeppesen, J., Ingvertsen, S., **Birch, H.**, Bergman, M., Panduro, T., Fratini, C., Jensen, M.B. (2009). Koblede afkoblinger. Vilkår for landskabsbaserede afkoblinger af regnvand i det københavnske kloakopland til Harrestrup Å.: Arbejdsrapport (Connected disconnections. Conditions for landscape based stormwater handling in the Copenhagen sewer catchment to Harrestrup Å: Working report). By&Landskab, Københavns Universitet. 71 s. http://2bg.dk/Internal_Workshop/2009-12-03-KE/2BG_HarrestrupAa_Booklet_web.pdf

Fryd, O., Backhaus, A., **Birch, H.**, Fratini, C., Ingvertsen, S.T., Jeppesen, J., Panduro, T.E., Roldin, M.K., Dam, T.E., Wenningsted-Torgard, R.M. and Jensen, M.B. (2012). Potentials and limitations for Water Sensitive Urban Design in Copenhagen: a multidisciplinary case study. Paper presented at the *7th International Conference on Water Sensitive Urban Design, Melbourne, Australia, 21-23 february 2012*

Jensen, M.B., Fryd, O., Backhaus, A., Ingvertsen, S.T., Pauleit, S., Dam, T.E., Bergman, M., **Birch, H.** and Mikkelsen, P.S. (2009). Holland: Landskabsbaseret afvanding (The Netherlands: Landscape based drainage). *Teknik & Miljø: Stads og Havneingeniøren*. 38-40.

Lützhøft, H.-C.H., **Birch, H.**, Eriksson, E. and Mikkelsen, P.S. (2011). Comparing chemical analysis with literature studies to identify micropollutants in a catchment of Copenhagen (DK). *In Proceedings of the 12th International Conference on Urban Drainage, Porto Alegre, Rio Grande do Sul, Brazil, 11th-16th September 2011*. Full paper: PAP005319. 8 p.

Pettersson, M., De Keyser, W., **Birch, H.**, Holten Lützhøft, H.-C., Gevaert, V., Cerk, M., Benedetti, L., and Vanrolleghem, P.A., (2010). Strategies for Monitoring of Priority Pollutant Emission Barriers. ScorePP project deliverable D7.5, 66 p. (available at www.scorepp.eu).

Sharma, A.K., Vezzaro, L., **Birch, H.** and Mikkelsen, P.S. (2011). Effect of climate change on stormwater characteristics and treatment efficiencies of stormwater retention ponds. *In Proceedings of the 12th International Conference on Urban Drainage, Porto Alegre, Rio Grande do Sul, Brazil, 11th-16th September 2011*.Full paper: PAP005314. 8 p.

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Abstract

The European Water Framework Directive (WFD) from 2000 has put focus on the chemical status of surface waters by the specified Environmental Quality Standard (EQSs) and the requirements for monitoring of surface water quality throughout Europe. When considering the water quality of urban stormwater runoff it is evident that surface waters receiving large amount of urban stormwater runoff will be at risk of failing to meet the EQSs. Therefore stormwater treatment is crucial. However, as stormwater quality varies orders of magnitude between sites, stormwater monitoring is important in order to design the right treatment level to protect surface waters. Stormwater runoff is very dynamic both quality and quantity wise. In order to optimize the sampling of such phenomena, advanced sampling equipment is required. Such equipment is expensive, and furthermore, it is time consuming to conduct the sampling campaigns. Therefore this PhD project aimed at improving monitoring programs for priority pollutants in stormwater runoff.

By comparing results from a literature study and a screening campaign to the EQSs, it was found that heavy metals (especially Cu and Zn), polyaromatic hydrocarbons (PAHs), Di(2-ethylhexyl)-phthalate (DEHP) and pesticides were the main pollutants of general concern in stormwater runoff and of concern at the studied catchment (glyphosate was found to be the most relevant pesticide in a Copenhagen setting). These priority pollutants are therefore relevant to monitor in stormwater discharges.

Sorption of pollutants to particulate matter and dissolved organic carbon is important for both the toxicity of the pollutants and for removal in stormwater treatment systems. Furthermore sorption is important for sampling using the most common types of passive samplers, which are based on uptake of analytes by diffusion, since they only sample the freely dissolved and labile fraction of analytes. Passive dosing was therefore developed during this PhD project as an easy, fast and precise method for partition measurements of hydrophobic organic compounds (HOC) in aqueous samples such as stormwater runoff. The principle of the method is that the freely dissolved concentration of the HOC is controlled by partitioning from a pre-loaded polymer and the total concentration in the sample at equilibrium is measured. Partition measurements in stormwater runoff samples revealed a partition ratio log K_{TSS} for fluoranthene of 4.59, and free

fractions in stormwater runoff of 0.04-0.5. The partition ratio can be used in modeling of stormwater treatment systems. The passive dosing method can be used for surface water monitoring to relate freely dissolved concentrations to total concentrations.

For stormwater monitoring, diffusion based passive samplers are not appropriate to use. The reason is that the sampler measures time-weighted concentrations over periods of weeks to months with no regard to whether it rains or not. Therefore a flow-through passive sampler, SorbiCell, was tested. It consists of a cartridge containing a sorbent and was installed directly in the stormwater drainage ditch letting the momentum from the water velocity force water through the sampler. This novel installation method ensures sampling mainly during runoff events and dependant on the velocity of the runoff. Even though a filter prevented large particles from entering the sampler, it revealed concentrations comparable to volume proportional total concentrations measured in stormwater runoff and modeled using a dynamic stormwater quality model. There are still many questions and assumptions when using this installation method. However it has potential for monitoring the load of priority pollutants to surface waters from the large amounts of stormwater discharge points often contributing to the deterioration of the water quality.

When evaluating the pollutant level at specific sites based on measurements, an interpretation of the system is always involved. This interpretation can be formulated in stormwater quality models. Event mean concentrations (EMCs) are often found to follow a lognormal distribution. However more complicated models including dynamics of accumulation in the catchment and influence of rain characteristics on the runoff concentrations can also be used. The advantage of using models for monitoring purposes is that information about the system beyond the time interval of sampling can be obtained based on knowledge of processes and observed patterns. It was found here that model prediction bounds for annual average concentrations obtained by a dynamic stormwater quality model were narrower than uncertainty on the mean when assuming lognormal distribution of EMCs. Furthermore, the use of passive sampler measurements in combination with volume proportional measurements for calibration reduced the model prediction bounds on annual average concentrations more than simply increasing the number of volume proportional samples. This work demonstrated how models and passive samplers can be used for monitoring purposes.

Dansk Sammenfatning

Vandrammedirektivet fra år 2000 har sat fokus på den kemiske vandkvalitet af overfladevand ved at definere vandkvalitetskriterier og krav om overvågning af kvaliteten af overfladevand i Europa. Det er imidlertid klart når man ser på kvaliteten af regnvandsafstrømning, at overfladevand der tilføres store mængder regnvandsafstrømning fra byområder vil risikere ikke at kunne overholde disse kvalitetskrav. Derfor er rensning af regnvandsafstrømning vigtig. Men eftersom kvaliteten af regnvandsafstrømning varierer størrelsesordner mellem oplande, er målekampagner vigtige for at kunne finde det rigtige rensningsniveau til at beskytte overfladevandet. Regnvandsafstrømning er meget dynamisk både mht. kvalitet og kvantitet. Derfor er avanceret prøvetagningsudstyr nødvendigt. Dette er dyrt, og prøvetagning er derudover knyttet til et højt tidsforbrug. Formålet med denne PhD var derfor at forbedre prøvetagningsprogrammer for miljøfremmede stoffer i regnvandsafstrømning.

Ved at sammenligne resultater fra litteraturen og en screeningsmålekampagne med kvalitetskriterierne, blev det konkluderet at tungmetaller (specielt Cu og Zn), polyaromatiske hydrocarboner, Di(2-ethylhexyl)-phthalate (DEHP) og pesticider er de primære problematiske miljøfremmede stoffer generelt i regnvandsafstrømning såvel som i de oplande der indgik i analysen (glyphosat var det mest relevante pesticid i Københavnsområdet). Disse stoffer er derfor relevante at overvåge i regnvandsafstrømning.

Sorption af miljøfremmede stoffer til partikler og opløst organisk materiale er vigtigt for både toksiciteten af stoffet og fjernelsen i bassiner og andre metoder til rensning af regnvand. Derudover er sorption vigtig når de mest udbredte typer af passive samplere benyttes. De optager nemlig stoffer ved diffusion, og optager derfor kun den totalt opløste del. Passive dosing blev udviklet som en enkel, hurtig og præcis måde til at måle fordeling af hydrofobe organiske stoffer i vandige prøver så som regnvandsafstrømning. Princippet i metoden er at den frit opløste koncentration af stoffet bliver styret af en ligevægt med en polymer der indeholder stoffet. Den totale koncentration i prøven ved ligevægt bliver efterfølgende målt. Fordelingsmålinger i regnvandsafstrømning viste en fordelingsligevægt, log K_{TSS}, for fluoranthene på 4.59, og frit opløste koncentrationer i regnvandsafstrømning på 4 - 50%. Passive dosing metoden kan

bruges til overvågningsprogrammer for overfladevand når koncentration af frit opløste stoffer skal relateres til totale koncentrationer.

Passive samplere som er baseret på diffusion er imidlertid ikke velegnede til at bruge til overvågning af regnvandsafstrømning. Det skyldes det faktum at denne type passive samplere måler tidsvægtet over tidsperioder på uger til måneder uden hensyn til om det rent faktisk regner eller ej. Derfor blev en passiv sampler der opsamler stof som funktion af vandgennemstrømningen, SorbiCell, testet. Den består af et hylster med en sorbent i til at opfange stoffer når vand passerer gennem hylsteret. Den blev installeret direkte i regnvandsgrøften på en sådan måde at vandhastigheden af det strømmende vand pressede vand gennem sampleren. Denne metode sikrer prøvetagning primært ved afstrømning og afhængig af vandets hastighed. Selv om et filter forhindrede store partikler i at komme ind i sampleren, målte den passive sampler koncentrationer svarende til totale koncentrationer i volumen proportionelle prøver af regnvandsafstrømningen. Der er stadig mange spørgsmål og antagelser når den passive sampler bruges med denne installationsmetode. Den har imidlertid et stort potentiale ved overvågning af belastningen af overfladevand med miljøfremmede stoffer fra regnvand fra en stor mængde udledningspunkter og oplande.

Når koncentrationsniveauet et specifikt sted skal vurderes baseret på målinger, er det altid baseret på en bestemt forståelse af systemet. Denne forståelse kan formuleres i modeller af kvaliteten af regnafstrømning. Hændelsesmiddel-koncentrationer følger ofte en lognormal fordeling. Mere komplicerede modeller, som tager højde for akkumulation af stofferne på overflader og indflydelsen af regnintensitet og varighed på koncentrationen i afstrømningen, kan også benyttes. Fordelen ved at bruge modeller til overvågning er at de giver information om systemet ud over den aktuelle måleperiode baseret på viden om processer og observerede mønstre. I dette arbejde var usikkerhedsintervallet på årsgennemsnittet mindre når en dynamisk afstrømningsmodel blev brugt end usikkerheden på gennemsnittet af en lognormal fordeling af hændelsesmiddelkoncentrationer. Brug af målinger med passive samplere kombineret med volumen proportionelle prøver til kalibrering af modellen reducerede usikkkerhedsintervallet på årsgennemsnittet mere end ved at bruge en større mængde volumen proportionelle prøver til kalibrering. Dette arbejde viste hvordan modeller og passive samplere kan bruges i overvågningen

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1 Introduction

1.1 The challenge of monitoring priority pollutants in stormwater runoff

Increased urbanization has many effects on the environment. One of these is the impact on the natural water cycle. This includes impacts on the quantity and quality of the water reaching the lakes and streams. In the beginning of the last century the largest impacts on the quality of urban surface waters was caused by untreated wastewater being discharged directly. As wastewater treatment plants are now handling wastewater in urban areas in Europe focus has changed to discharges of stormwater (also often called stormwater runoff) and combined sewer overflows which, during rain, contribute substantially to the pollution of surface waters (Clark et al., 2008; Eriksson et al., 2007b; Göbel et al., 2007; Kjølholt et al., 2007).

In Europe, the water quality of surface waters has been brought into focus by the Water Framework Directive (WFD) from 2000 (European Commission, 2000). The Water Framework Directive aims at improving the ecological status of inland and coastal waters by 2015. This includes reducing the pollution of surface waters with 45 identified priority substances and phasing out emissions, discharges and losses of 17 of these, which are identified as priority hazardous substances. For these substances environmental quality standards (EQS) have been defined as annual average (AA-EQS) and maximum allowable concentrations (MAC-EQS) (European Commission, 2008). These quality standards are regularly updated and a new version including 15 additional priority substances is presently proposed (European Commission, 2011). For heavy metals the EQSs are defined for dissolved concentrations, reflecting the fact that this is the fraction of the pollutants responsible for the toxic effect. However for organic pollutants, the EQSs are defined for total concentrations, reflecting the lack of knowledge about partitioning of organic pollutants in natural environments.

The EQSs are in Denmark implemented in the executive order 1022 (Danish Ministry of the Environment, 2010). Compared to the WFD it includes more substances and more stringent criteria for some of the substances. It is used for discharge permits with the exception of discharges of ‘normally loaded’ stormwater. However, even though stormwater discharge permits are not

targeted, the WFD EQSs are indirectly applicable for stormwater discharges since they apply to the recipients.

The WFD also includes requirements for monitoring of the ecological and chemical status of the water bodies in all member states (European Commission, 2000). The monitoring includes the chemical status regarding priority substances and other relevant pollutants (in this thesis the term priority pollutants, PPs, will be used to denote all the relevant pollutants, organic compounds as well as heavy metals, whether included in the WFD or not). Monitoring of stormwater is not specifically required in the WFD. However, for many surface waters stormwater is a major contributor of PPs. Therefore these discharges will have to be treated in some way. In order to design the right level of treatment, monitoring of stormwater is necessary (Ingvertsen et al., 2011).

The traditional methods for taking water samples include methods from manual 'grab sampling' to time, flow or volume proportional sampling using automatic samplers. The samples are then taken to the laboratory for analysis, which can be chemical analysis and/or toxicity tests. A range of alternative sampling methods have been developed in the later years focusing on *in situ* extraction (bringing only the extract/sorbent to the lab for analysis) or *in situ* measurements (see Table 1). The use of these alternative sampling methods for monitoring purposes are discussed and exemplified in Allan et al. (2006a; 2006b). Some methods are appropriate for point measurements in time (instant measurements) while other methods are suitable for time/volume/flow proportional sampling (Table 1).

Table 1: Classification of sampling methods according to whether the method target pollutant concentrations or toxicity in samples, *in situ* analysis or laboratory analysis and instant or average concentrations/effects.

	Pollutant concentrations		**Toxicity measurements**	
	Instant	**Average**	**Instant**	**Average**
Extraction and analysis in lab	Grab sampling	Time, volume and flow proportional sampling	Bioassays (performed on grab or time/flow proportional samples)	
***In situ* extraction or measurement**	Passive samplers (equilibrium) Immunoassays Sensors	Passive samplers (kinetic)	Biological early warning systems	Biomarkers

The advantage of using measurements of toxicity is that the combined effect of all the pollutants is measured directly. However toxicity measurements alone do not show which pollutants are responsible for the effects seen. The advantages of pollutant concentration measurements are that legislation is based on chemical concentrations and that the pollutants can be linked to sources. Furthermore sources can be regulated and remediating actions can also be evaluated on the basis of change in pollutant concentrations. The disadvantage is that important pollutants can be 'missed' because they were not looked for and that combined effects of multiple PPs are not taken into consideration.

The challenge when monitoring stormwater runoff is the very dynamic nature of the system. Both the quantity and the quality of the stormwater vary orders of magnitudes between different sites (Göbel et al., 2007; Maestre and Pitt, 2005). Furthermore the variations over time at each location can also be huge (Lee et al., 2007). This challenge has traditionally been approached by using flow- or volume proportional sampling equipment. By sampling a number of different rain events covering seasonal variations, a range of event mean concentrations (EMCs) can be found. These EMCs can then be compiled into a single site mean concentration (SMC) which can be used to evaluate the load of pollutants from the discharge point (Mourad et al., 2005). This approach is both time consuming and costly, especially if a broad range of PPs, for which chemical analysis can be very expensive, have to be monitored. The many novel passive sampling techniques have only to a small extent been used in stormwater drainage systems (e.g. **Paper IV**, Blom et al. (2002) and Komarova et al. (2006)). Effort have also been put in developing stormwater quality models for PPs in order to expand the knowledge of the system beyond the actual sampled events (Vezzaro et al., 2012; Vezzaro and Mikkelsen, 2012). However the role of passive samplers and stormwater models for monitoring purposes has not yet been investigated.

1.2 Aims and research questions

The aim of this thesis is to investigate the possibility to improve monitoring programs for PPs in stormwater runoff. The main hypothesis of the thesis is that a combination of active and passive sampling with stormwater quality modeling can be used for monitoring concentrations and loads of PPs in stormwater in a smarter way than the traditional monitoring programs. This will lead to lower cost and/or deeper knowledge gained by the monitoring programs by including more substances or sites in the program. This is greatly needed since the amount

of pollutants targeted in legislation is increasing whereas monitoring budgets are strict or being cut in many countries.

The following research questions are studied in this thesis:

1. Which pollutants are relevant to monitor in stormwater?
2. How can the sorption capacity of stormwater be characterized in order to relate total concentrations (targeted in regulation of organic substances) to dissolved concentrations (responsible for toxic effects) and better predict the fate of priority pollutants in stormwater treatment systems?
3. Can passive samplers be used for monitoring of stormwater discharges? Which advantages, disadvantages and uncertainties do they have?
4. How can models in combination with new technological sampling techniques improve monitoring of dynamic discharges from urban areas?

1.3 Methods and overview of thesis

The methods used to approach these research questions included literature studies, field work, development of an analytical method and stormwater quality modeling. Figure 1 shows a conceptual drawing of a stormwater drainage system where roof and road runoff is collected in storm sewers and treated in a retention pond before discharge to a stream. The drawing shows how the stormwater system was approached at different levels in this PhD project and thesis: overall monitoring strategies involving the whole drainage system and surface waters (section 2 and 6), evaluating pollution and modeling on a catchment level (section 3 and 6), looking into specific sampling techniques for stormwater (section 5), and focusing on partitioning of organic pollutants in stormwater (section 4).

The thesis starts with a general presentation of different types of monitoring defined in the WFD (Section 2).

In section 3, the occurrence and relevance of pollutants in stormwater is investigated. This includes among others the results from a screening campaign conducted in Copenhagen (**Paper I**).

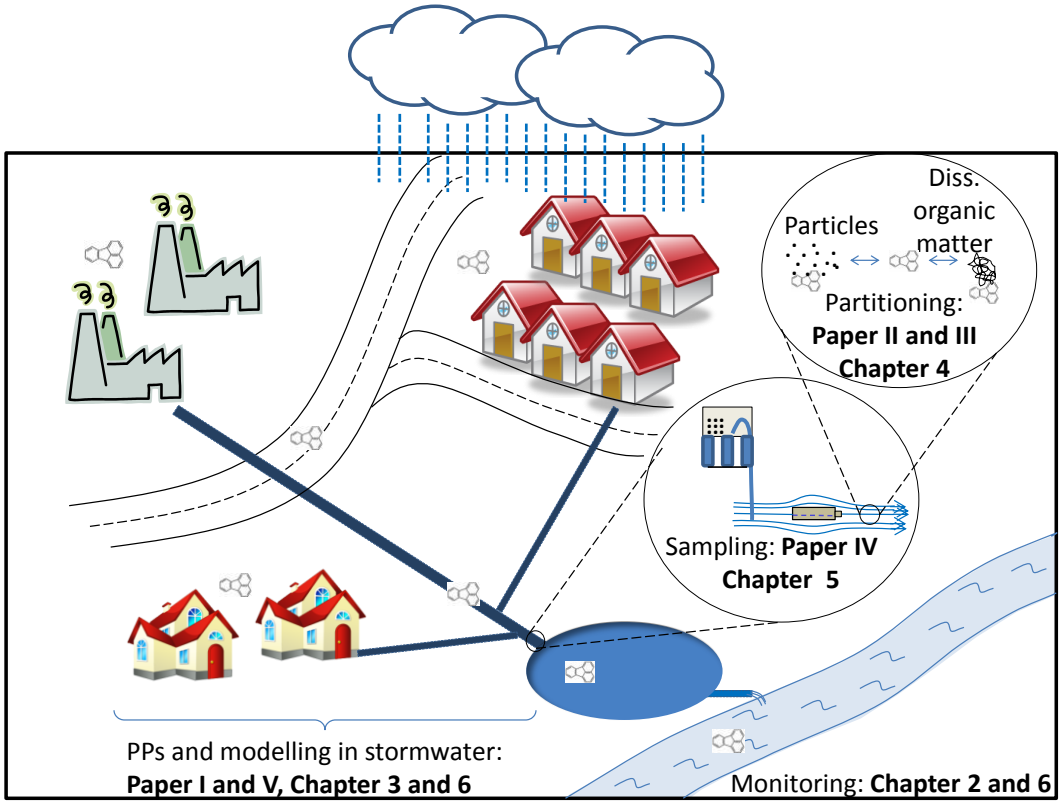

Figure 1: Conceptual sketch of a stormwater drainage system.

An important characteristic of the fate of PPs is the sorption to particulate and dissolved matter. Partitioning is discussed in Section 4. This includes a new analytical technique for partitioning measurements of hydrophobic organic compounds (HOCs), passive dosing, which was developed during the PhD (**Paper II**). The importance of partitioning in stormwater runoff is also discussed based on application of the method to stormwater runoff samples (**Paper III**).

Sampling of stormwater runoff is discussed in section 5. Specific focus is put on passive sampling methods, including tests of a flow-through passive sampler which was installed for velocity dependant sampling (**Paper IV**).

This is wrapped up by section 6, where the role of the passive samplers, passive dosing and modeling for monitoring purposes is discussed. This section also includes a discussion of stormwater modeling in general.

1.4 Field work: locations and sampling

Two main sampling campaigns were completed during the PhD project, an initial screening campaign and an extensive sampling campaign in Albertlund. Furthermore samples from a retention pond in Chassieu in France were used.

The screening campaign consisted of one grab/precipitation dependant/volume proportional sample in six storm sewers (four different sites) and one CSO (Table 2).

After the initial screening campaign and method development, field work was focused in the catchment in Albertslund (Fabriksparken) where stormwater runoff from an industrial/residential area is treated in a retention pond (basin K) before discharge to a stream (Harrestrup Å). The events sampled during this sampling campaign are shown in Figure 2.

Table 2. Description of the sites, samples and rain events studied in the initial screening campaign (from **Paper I**).

Town	**Tårnby**	**Tårnby**	**Albertslund**	**Glostrup**			**Gentofte**
Sites	**Byparken**	**Digevej**	**Fabriks-parken**	**Ejby mose**			**Scher-figsvej**
Sewer type	Storm sewer	Storm sewer	Storm sewer	Storm sewer			CSO[1]
Impervious area	1.3 ha	9.4 ha	56 ha	13 ha	60 ha	5 ha	1100 ha
Catchment type[2]	Roads	Res. and metro	Ind. & res.	Res.	Ind. & road	Res. & road	Res. & roads & drains
Treatment	Grit chamber	Grit chamber	Oil sep.[4]	Oil sep.[4]	Oil sep.[4]	Oil sep.[4]	-
Sample type	Grab	Grab	Grab	Precipitation dependant[5]			Volume proportional
Date	10/15 2008	11/18 2008	11/18 2008	09/02 - 09/03 2009			09/30 2008
Rain depth[6]	2.3 mm	1 mm	5.7 mm	11 mm			6.4 mm
Duration[6]	3 hours	30 min	3 hours	16 h			23 h
Antecedent dwp[7]	9 days	36 hours	36 hours	36 hours			7 days

[1]Combined Sewer Overflow, [2]Res. = residential, Ind = Industrial, [3]natural wetland, [4]separator, [5]Samples are taken depending on precipitation measured in a rain gauge at the site, [6]For grab samples the depth and duration refers to rain depth and how long time it had rained when the grab sample was taken, not the total rain event depth and duration, [7]dwp=dry weather period.

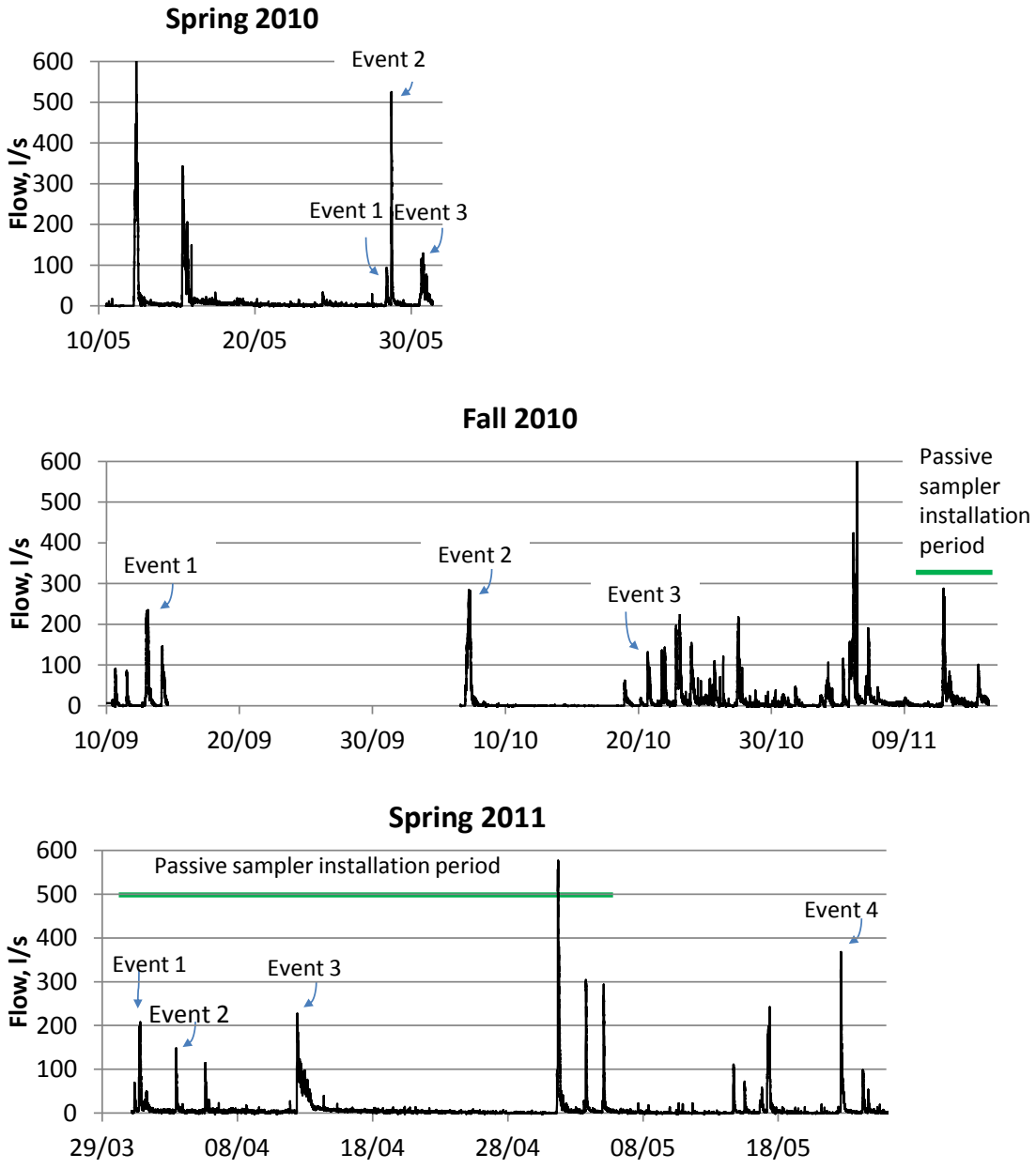

Figure 2: Flow during the extensive sampling campaign in Albertslund. The three events sampled using autosamplers during spring 2010 and fall 2010 and the four events during spring 2011 are indicated. Two passive sampler installation periods are shown as well.

In total 10 events were sampled using autosamplers to sample volume proportionally in the inlet to the pond and time proportionally in the outlet from the pond. During two periods passive samplers were also installed here (see Figure 2).

The samples collected in Albertslund were used for multiple purposes. Partitioning of fluoranthene in stormwater runoff were measured in samples from this catchment (events 1, 3 and 4 from spring 2011), using the passive dosing method (**Paper III**). Initial tests of a flow-through passive sampler were performed during fall 2010, and during spring 2011 volume proportional sampling were used in parallel with passive sampling in order to compare the two methods (**Paper IV**). These samples were furthermore used to evaluate different sampling strategies by applying a stormwater runoff quality model (**Paper V**). Spring and fall events from 2010 were used to calibrate the model, and the four events and passive samplers from spring 2011 were used to evaluate hypothetical sampling strategies which could be adopted for further analysis of the catchment.

The retention pond in Chassieu in France receives stormwater from an industrial catchment with an impervious area of 139 ha (Bertrand-Krajewski et al., 2008). Partitioning of fluoranthene was measured in three composite stormwater samples from the inlet and the outlet of the retention pond. The results are compared to the results from Albertlund in this thesis (Section 4.3).

2 Monitoring

2.1 Water Framework Directive

Monitoring of PPs in the environment is closely connected with requirements in the legislation. Therefore, the substances included in the WFD, their AA-EQS and MAC-EQS values and the requirements for monitoring are drivers for establishing monitoring campaigns in Europe. In the WFD three types of monitoring are defined: surveillance, operational and investigative monitoring. The aims of these three types of monitoring are listed in Figure 3.

Aims of surveillance monitoring:
- supplementing and validating the impact assessment,
- efficient and effective design of future monitoring programmes,
- assessment of long-term changes in natural conditions,
- assessment of long-term changes resulting from widespread anthropogenic activity.

Aims of operational monitoring:
- establish the status of those bodies identified as being at risk of failing to meet their environmental objectives
- assess any changes in the status of such bodies resulting from the programmes of measures.

Investigative monitoring should be carried out:
- where the reason for any exceedance is unknown,
- where surveillance monitoring indicates that the objectives set out for a body of water are not likely to be achieved and operational monitoring has not already been established, in order to ascertain the causes of a water body or water bodies failing to achieve the environmental objectives,
- to ascertain the magnitude and impacts of accidental pollution

Figure 3: The aims of the three types of monitoring programs as defined in the WFD (European Commission, 2000).

Requirements for sampling stated in the WFD are that sampling should conform to the ISO-guidelines and that for priority substances a frequency of one sample per month is used as standard. For analysis, "the minimum performance criteria for all methods of analysis applied are based on an uncertainty of measurement of 50% or below estimated at the level of relevant EQS and a limit of quantification equal or below a value of 30% of the relevant EQS" (European Commission, 2009). The WFD opens up for variations in sampling methods, frequencies and local considerations e.g. by saying that the frequency should be chosen "so as to provide sufficient data for a reliable assessment of the status of the relevant quality element. As a guideline, monitoring should take place at

intervals not exceeding those shown … unless greater intervals would be justified…"(European Commission, 2000). However the role of passive samplers and stormwater models for monitoring purposes has not been established. The WFD monitoring requirements are illustrated in Figure 4.

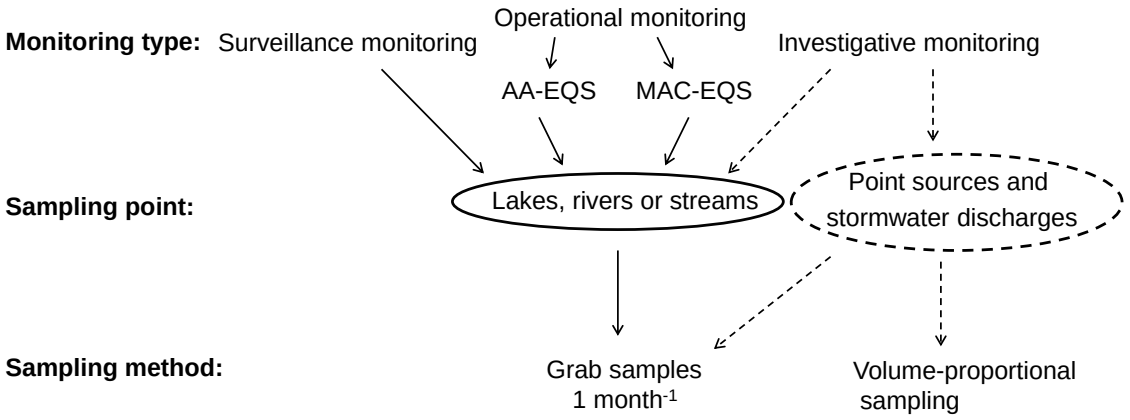

Figure 4: Monitoring strategies as suggested in the water framework directive (European Commission, 2000). Dotted lines: not specifically mentioned in the WFD.

Surveillance and operational monitoring both target the status of the water bodies. Therefore the monitoring points are within the respective lakes, rivers or streams. Long term changes in the chemical status of water bodies with relatively slow changes in concentrations can be assessed by taking grab samples, since a grab sample in this case can represent the concentration in the water body during a time period. However, care should be taken when defining the monitoring point in surface waters impacted by urban runoff, since stormwater discharges are so dynamic that one sample per month (as suggested in the WFD) in no reasonable way can represent the level of pollution if the monitoring point is located close to a discharge point.

Estimating long term changes in water bodies with fast changes of water flow and quality, such as streams or rivers, by taking the required amount of grab samples is not straight forward. For analytes showing a strong daily pattern, different conclusions can be drawn depending on when the samples are taken, during day or night, dry or wet weather etc. (Hazelton, 1998). The sampling strategy should therefore be determined depending on the use pattern for the PPs in question. Herbicides showing a spring first flush pattern can e.g. be monitored

by sampling more frequently in spring and early summer months and assuming zero concentrations during the rest of the year (Battaglin and Hay, 1996), on the other hand Fletcher and Deletic (2007) found that for evaluating the TSS loads in rivers and streams sampling intervals should be 3 days or less in order to ensure absolute errors below 10%.

Operational monitoring must relate to the AA-EQSs and MAC-EQSs when establishing the chemical status of the water bodies. Operational monitoring strategies aimed at finding annual average concentrations are comparable to surveillance monitoring strategies for finding long-term changes of the chemical status of surface waters. In the definition of the MAC-EQS, the requirement is that none of the samples taken during the monitoring program are allowed to exceed the MAC-EQS. "However ... Member States may introduce statistical methods, such as a percentile calculation, to ensure an acceptable level of confidence and precision for determining compliance with the MAC-EQS" (European Commission, 2008).

Investigative monitoring is by nature different from the two other types of monitoring. The aim is not to establish the status but to find out why a good status is not achieved. The investigative monitoring is therefore not described as detailed as the two other monitoring strategies. In investigative monitoring it can be relevant to sample stormwater discharges and point sources. Stormwater discharges and point sources are much more dynamic in nature than most water bodies. In a comprehensive study of sampling approaches by Ackerman et al. (2011), it was concluded that the most efficient sampling method for stormwater monitoring was volume proportional sampling (using 10 sub-samples per composite sample), with variable sample pacing to ensure that the entire storm was captured.

2.2 Monitoring priority pollutants in stormwater runoff

As already mentioned, monitoring of stormwater can be used in WFD investigative monitoring to find out why the receiving waters do not have good chemical status. However, there are other reasons to monitor stormwater quality. When looking at the water quality of stormwater runoff it is evident that there is a need for treatment of stormwater in order to comply with the EQSs in most receiving waters (especially water bodies which receive a large fraction of urban stormwater runoff). One approach is to use standard criteria for designing

stormwater treatment systems such as ‘best available technology’. However, it is also expensive to oversize treatment systems or to apply treatment that may not be necessary at all locations. Monitoring can therefore help in designing appropriate treatment systems for stormwater runoff. Furthermore, in Denmark, the water utilities who are responsible for management of stormwater runoff, are privatized and no longer part of the municipalities. As the responsibility of the water bodies belong to the municipality, the municipality sets requirements for the quality of stormwater discharged to the water bodies. It can therefore be important for the water utilities to be able to document the quality of the water they discharge to the receiving waters.

3 Priority pollutants in stormwater

3.1 Selection of pollutants for monitoring

Different approaches are followed when choosing which pollutants to include in monitoring programs for identification of pollutant concentration levels. Five examples of approaches are presented here: the scientific approach CHIAT, the approach used in a research project ESPRIT, the Danish national monitoring program NOVANA, the US EPA monitoring program for water quality and the approach used for a screening campaign in **Paper I**. A minimum data set for evaluating performance of stormwater treatment systems have also been identified (Ingvertsen et al., 2011).

The chemical hazard identification and assessment tool (CHIAT) is a scientific approach to select PPs (Eriksson et al., 2005). The CHIAT method covers source characterization, exposure identification, hazard identification and assessment as well as expert judgement. A tool for source characterization has been developed in the EU project ScorePP. It consists of a database of sources, release factors and patterns compiled for selected priority substances from the WFD (www.scorepp.eu) (Lützhøft et al., 2012). However, the source characterization in the CHIAT method is not limited to regulated pollutant, but aims at a broad identification of sources and potential pollutants. The hazard identification can be evaluated using the RICH method (ranking and identification of chemical hazards) (Baun et al., 2008). In the RICH method, pollutants are ranked based on their inherent properties. The CHIAT method was used to select a list of stormwater PPs in the EU Daywater project (Eriksson et al., 2007b).

One of the research projects on stormwater PPs conducted during the same period as this PhD project is the ESPRIT project, where the aim was to identify, evaluate and characterize priority substances from the EU WFD in stormwater. Legal considerations was therefore the (only) criterion for selecting pollutants to monitor (Bertrand-Krajewski et al., 2008).

In the Danish national monitoring program, substances were selected to 'meet the international obligations and at the same time provide an overview over the inputs from the different types of point sources' (Danish Environmental Protection Agency, 2000). Here legal considerations are also important; however the criteria followed for the specific choices of pollutants have not been stated.

The approach set out by the US EPA for choosing indicators to include in water quality monitoring programs is stated this way: “Because limited resources affect the design of water quality monitoring programs, the State should use a tiered approach to monitoring that includes a core set of baseline indicators selected to represent each applicable designated use, plus supplemental indicators selected according to site-specific or project-specific decision criteria” (US EPA, 2003). Thus overall considerations as well as local considerations are taken into account, and the economical aspect is also pointed out.

The criteria used when selecting pollutants for a screening campaign of pollutants in stormwater runoff are described in **Paper I** (see Figure 5). Three criteria were used: legislation, local considerations and practical aspects. Similar to the ESPRIT project and the Danish national monitoring program, the priority substances listed in the EQS directive (European Commission, 2008) were used as a basis for the selection of PPs.

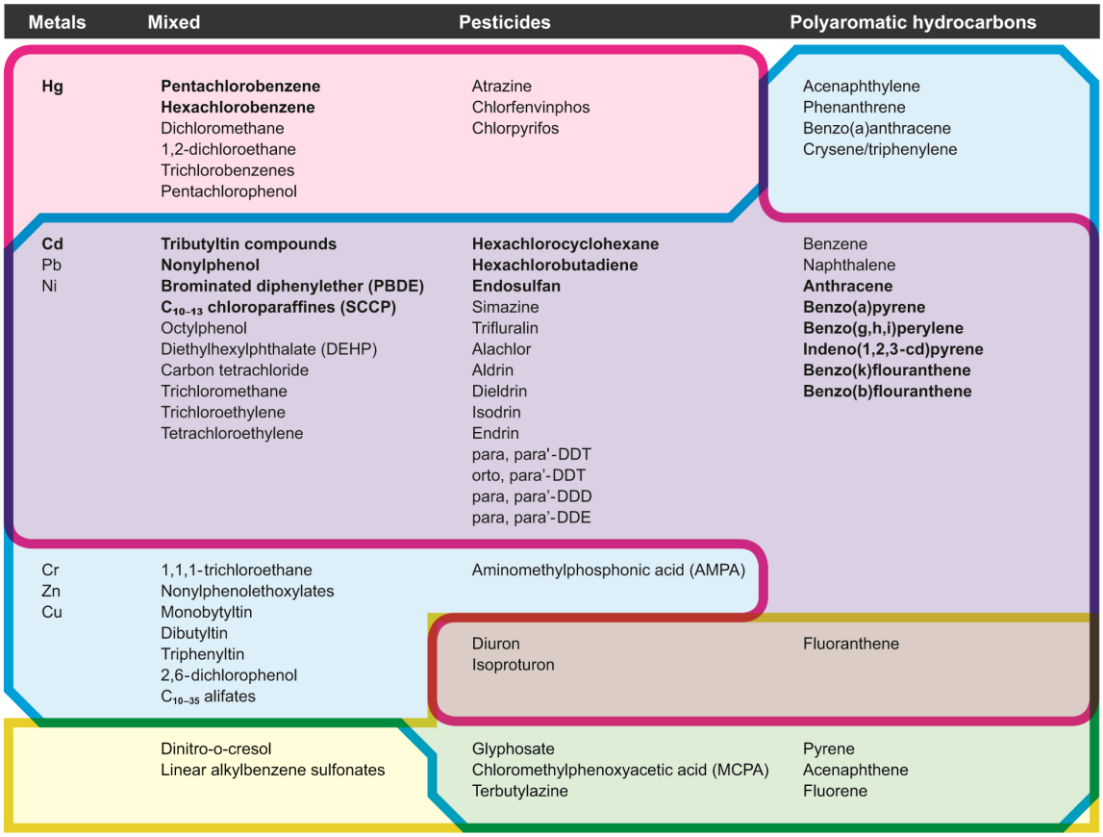

Figure 5: Selection of priority pollutants for monitoring (**Paper I**). EU priority substances and priority hazardous substances (bold) are shown in the red rounded shape. Pollutants found in an earlier risk assessment of a catchment in Copenhagen are shown in the yellow shape. Pollutants selected in the present study based on practical limitations are shown in the blue shape.

As in the approach used by the US EPA, this basic list was supplemented with local knowledge, in this case a risk assessment performed in the area and knowledge on the use of pesticides (Eriksson et al., 2007a). However, the practical side is often the limiting factor when designing monitoring programs. Therefore considerations of the budget size, which analytes were included in the same analyses, detection limits and how much sampling volume was needed for each analysis was also taken into account.

From these monitoring campaigns it is therefore seen, that the important factors to consider when choosing PPs for monitoring are: scientific knowledge on pollutants (e.g. inherent properties as used in the RICH method), relevant legislation, local considerations (sources and earlier findings) and practical issues (economy, analytical considerations, sampling etc.). The importance of each factor depends on the local settings and aims. However, when all these factors are considered, selection can be done in a deliberate manner where the monitoring program is limited to the important pollutants.

3.2 Sources and occurrence of pollutants in stormwater

The main sources of pollution in stormwater are wet and dry deposition, activities in the catchment (e.g. traffic, application of pesticides, industrial activity) as well as release of pollutants from materials in contact with the water (see e.g. Eriksson et al. (2005)). The sources to the PPs can be activities outside of the local catchment since dry and wet deposition can transport PPs over short and long distances. Traffic sources covers wear and tear of tires, asphalt, brakes, undercoating, and combustion products from exhaust as well as drip losses (e.g. Sörme and Lagerkvist (2002)). Materials in contact with the water include asphalt, roof materials, paints, concrete etc. These materials have been shown to leak pollutants such as biocides (Burkhardt et al., 2011; Schoknecht et al., 2009; Skarzynska et al., 2007)

A large number of studies have investigated different pollutants in stormwater runoff. Over 650 organic pollutants and 30 metals and inorganic metals have been identified as potential stormwater pollutants (Eriksson et al., 2007b; Ledin et al., 2004). There is a varying level of knowledge about the occurrence of these pollutants in stormwater. For some parameters such as suspended solids, organic matter, nutrients and heavy metals, a fair amount of data can be found in the

literature (Göbel et al., 2007; Ingvertsen et al., 2011), and they are also included in the National Stormwater Quality Database, NSQD, from the USA covering over 3700 storm events (Maestre and Pitt, 2005). For these parameters, concentrations have been compiled for different catchment types (Maestre and Pitt, 2005) and surface types (e.g. road and roof types) (Göbel et al., 2007; Skarzynska et al., 2007).

Information on organic compounds in stormwater is much scarcer than on suspended solids, organic matter, nutrients and heavy metals. Individual polyaromatic hydrocarbons (PAHs) have been investigated to some extent, while herbicides, pesticides and a range of other organic substances have only been measured in a few studies (Ingvertsen et al., 2011; Ledin et al., 2004; Skarzynska et al., 2007). Studies which include monitoring of a broad range of pollutants at the same location or time, e.g. the priority substances regulated through the WFD, are only recently reported and currently being conducted. This includes the screening campaign reported in **Paper I**, which included a broad range of pollutants at five different locations (4 stormwater discharge sites and 1 combined sewer overflow). In France, large research projects measuring PPs in atmospheric deposition and stormwater are under way (Bertrand-Krajewski et al., 2008; Sebastian et al., 2011), and measurements of PPs in surface waters and stormwater have been reported (Gasperi et al., 2009; Zgheib et al., 2011).

In Table 3 an overview from literature of concentration ranges of PPs in stormwater is shown (basic parameters such as TSS, organic matter and nutrients are not included). Different levels of smoothing of the data have been used in the different reviews and studies: in some studies concentration ranges in single samples are averaged into EMCs for each event, and in other studies these are averaged to SMCs. For comparison, the MAC-EQS, and where this is not defined the AA-EQS are listed as well. Note that the EQS values for the heavy metals apply to measurements of filtered samples, while the literature listed here reports total concentrations (dissolved concentrations can vary from 90% to <10% depending on the heavy metal of interest (Ingvertsen et al., 2011)).

As mentioned earlier, the larger (review) studies by Maestre and Pitt (2005) and Göbel et al. (2007) include mainly information about heavy metals. As the study by Ledin et al. (2004) includes concentrations of samples rather than EMCs or SMCs, the range is broader than the other review studies, and extreme

concentrations are also included which are not representative of the general state of stormwater runoff. However it is evident that stormwater from some sites would require much treatment in order to comply with the guidelines in the recipients. A proposal for an update of the EQS directive (European Commission, 2011) lowers the EQSs for PAHs, brominated diphenylethers, lead and nickel compared to the existing EQSs (EC 2008) used in this PhD thesis (e.g. AA-EQS and MAC-EQS for fluoranthene is lowered from 0.1 and 1 µg/L to 0.0063 and 0.12 µg/L respectively), meaning that in the future it is anticipated to be even harder to comply with EQSs in surface waters.

Which pollutants are problematic in stormwater runoff depends on the actual location. However some pollutants are more general stormwater pollutants than others. The heavy metals have for a long time been in focus in stormwater runoff. Very high concentrations have been found in stormwater runoff compared with the EQSs for surface waters (Table 3). However, the concentrations measured in the screening study (**Paper I)** and in the stormwater pond in Albertslund (**Paper IV and V**), indicate that the heavy metals Cu and Zn, which are not strongly sorbed to particulate matter in stormwater (sorption of 10-95% have been found for Zn and 35-90% for Cu (Ingvertsen et al., 2011)), are most problematic in stormwater discharges at these sites.

PAHs in stormwater runoff are seen to exceed the EQSs in all studies. As PAHs are related to traffic and fireplaces these compounds are more generally found in stormwater runoff than other point source related compounds. Removal of PAHs in stormwater treatment facilities is therefore important.

Pesticides can be regulated through source control much easier than the PAHs. Many pesticides are regulated in use. Pesticides which are banned are often only found in low concentrations in stormwater runoff. However, for many of the pesticides which are in use, and therefore found in higher concentrations, EQSs have not yet been established. In order to evaluate the effect of pesticides in stormwater runoff, toxicity data of the locally used pesticides have to be consulted.

Table 3: Concentration of selected priority pollutants in stormwater. The table is not exhaustive for constituents and studies.

Pollutant µg/l	Review studies (Maestre and Pitt, 2005)[a]	(Göbel et al., 2007)[b]	(Ledin et al., 2004)[c]	Broad studies (Zgheib et al., 2011)[d]	Paper I[e]	MAC-EQS/(AA-EQS)[f] WFD
Heavy metals						
Cd		0.2-13	<0.1-700	n.d.	0.11-0.63	0.45-1.5[g,h]
Cr		2-50	<0.5-4200	10-45	0.41-41.2	(3.4)[g,i]
Cu	0.6-1360	6-3416	<0.5-6800	50-220	22-255	(12)[g,i]
Ni	1-120	2-70	5-580	n.d.	0.93-40.5	(20)[g,i]
Pb	0.2-1200	2-525	<0.5-2764	25-129	9.8-72.4	(7.2)[g]
Zn	2-22500	15-4880	0-38061	130-520	74-244	(7.8)[g,i]
PAHs						
Naphthalene			0.006-49	0.088-0.175	<0.01-0.72	(2.4)
Acenaphtylene			<0.05-0.96	0.027-0.126	<0.01-0.039	
Acenaphthene			0.002-0.97	0.013-0.044	<0.01	
Fluorene			0.001-74	0.019-0.106	<0.01-0.028	
Phenanthrene			<0.01-1420	0.090.0.712	0.017-0.29	
Anthracene			<0.0001-147	0.016-0.096	0.012-0.084	0.4
Fluoranthene			0.009-1958	0.098-0.832	0.025-0.55	1
Pyrene			0.0001-120	0.100-1.223	0.034-0.56	
Benzo(a)anthracene			0.0003-54	0.037-0.298	<0.01-0.21	
Chrysen/triphenylene			<0.01-2271	0.088-0.655	<0.01-0.38	
Benzo(b+j+k)fluoranthene			<0.01-0.49	0.100-0.876	<0.01-1.0	(0.03)
Benzo(a)pyrene			0.00015-300	0.041-0.315	<0.01-0.31	0.1
Benzo(g,h,i)perylene			<0.01-710	0.071-0.569	<0.01-0.47	} (0.002)
Indeno(1,2,3-cd)pyrene			<0.01-1080	0.053-0.354	<0.01-0.39	
Dibenzo(a,h)anthracene			<0.01-83	0.021-0.096	<0.01	
Total PAH		0.24-17	<0.011-178		0.088-4.38	

Pesticides				
Glyphosate		<0.05-1.92	0.043-1.2	
AMPA		0.479-0.731	0.06-0.33	
Diuron	0.25-238.4	0.394-0.647	<0.01-0.055	1.8
Isoproturon	<0.05-0.079	0.004-0.082	<0.01-0.044	1.0
Terbutylazine	0.017-0.16		<0.01	
MCPA	0.009-0.13		<0.01-0.018	
Monobutyltin		0.091-0.120	0.035-0.048	
Dibutyltin		0.074-0.093	0.008-0.009	
TBT		0.050-0.078	<0.004	0.0015
Other organic substances				
Benzene	0.017-13	n.d.	<2	50
Nonylphenol	<0.04-23	1.595-9.17	<0.1-0.43	2.0
Octylphenolethoxylates			<0.5-12	(0.1)
DEHP	3.0-44	15.3-60.9	2.9-8.5	(1.3)
Trichloroethylene	0.036-7	n.d.	<0.02	(10)
Tetrachloroethylene	0.058-25	n.d.	<0.02	(10)
Chloroform	<0.1-12	n.d.	0.02	(2.5)

[a]The review reports range of site mean concentrations (SMCs) with a minimum number of events for each site of 3. [b]The review reports event mean concentrations (EMCs). [c]The review reports sample concentrations (all kind of samples). [d]The study reports EMCs. [e]The study reports grab samples and precipitation proportional samples. [f]maximum allowable concentration or annual average concentration from the water framework directive [g]filtered samples, [h]depending on the hardness of the water, [i]Danish EPA guidelines, n.d.: not detected. Blank cell = not included in the study.

There are many other organic pollutants which could be problematic at specific sites. However, DEHP is generally found in stormwater runoff. This is connected to the wide use of this plasticizer in plastic products which are exposed to weathering.

The main pollutants were therefore found to be the heavy metals Cu and Zn, the PAHs, pesticides in use (here Glyophosate was found) and the plasticizer DEHP.

4 Partitioning of priority pollutants in stormwater

Sorption of PPs to particulate matter and dissolved organic carbon (DOC) in stormwater is important for the toxicity, degradation and transport of PPs, and for removal in stormwater treatment systems.

4.1 General principles

Partitioning or speciation is the distribution of a compound between its chemical forms e.g. freely dissolved, ionic, complex-bound, particle-bound, bound to colloids and taken up in biota. The term speciation is often used when talking about metals, and the term partitioning when referring to organic compounds. The distribution is characterized by equilibrium constants, partition ratios or accumulation factors and depends on the compound as well as on the constituents in the system; ligands, organic substances, particles etc. (Figure 6). The speciation of metals and hydrophobic organic compounds are driven by different mechanisms. Freely dissolved metals are on ionic form and interact with other ions, macromolecules or colloids by forming complexes and with suspended organic and inorganic particles by sorption-desorption processes. Hydrophilic compounds can be either on ionic or non-ionic form, and can distribute between the different forms in a manner similar to metals. Hydrophobic organic compounds are not on the ionic form and do not form complexes but distribute among the organic phases of the system mainly by absorption and adsorption (if the compounds can be ionized, the ions can also form complexes in a manner similar to metals).

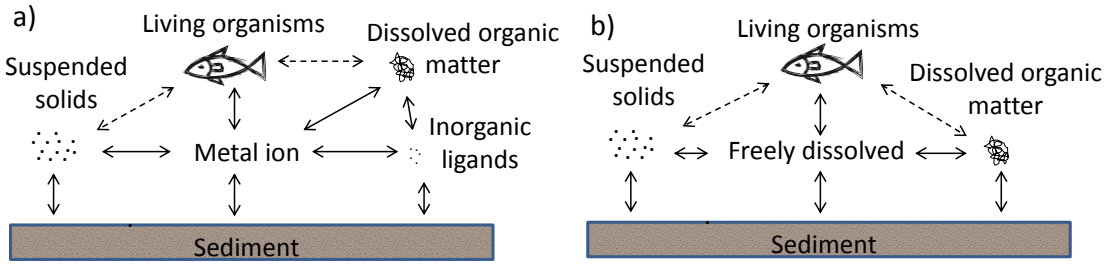

Figure 6: Speciation of metals (a) and hydrophobic organic compounds (b). Dashed arrows indicate that this uptake route is only relevant for some type of biota.

Kinetics of complexation and sorption are very important for speciation. Two different forms can be distinguished – labile and inert forms. Labile species are the forms which have relatively fast complexation or partitioning kinetics compared to the time-frame of the system, whereas inert forms have slow kinetics (species with kinetics in the same range as the time-frame of the system are called non-labile). Labile species are therefore in rapid equilibrium with each other whereas inert species do not obtain equilibrium and do not contribute noticeably to partitioning processes. As the time-scale of the system defines the frame for the equilibrium, species can be considered labile in one system and inert in another system.

Uptake of PPs in organisms and in many passive samplers is constricted to the freely dissolved and labile species. Exceptions from this and discussion of the uptake mechanisms of metals and organics in aquatic organisms is out of the scope of this thesis, but is discussed in more depth in e.g. Worms et al. (2006).

4.2 Methods for speciation and partitioning measurements

For characterization of speciation in aqueous samples it is necessary to be able to analytically distinguish the complexed and/or sorbed species from the freely dissolved compound. For metals, van Leeuwen et al. (2005) go into depth with the concept of dynamic speciation and the available sensors for metal speciation measurements. Since sorption is more important for HOCs than for hydrophilic compounds and most of the organic pollutants included in the WFD are hydrophobic, partition measurement methods will here be discussed with a focus on the HOCs.

Speciation of HOCs is theoretically not as complicated as for heavy metals because inorganic complexes can be neglected and because partitioning processes are well defined. However sorption processes with very slow kinetics (Jonker et al., 2005) or ‘trapping’ of compounds in some types of particles has been suggested for some HOCs making them unable to participate in the partitioning processes (Jonker and Koelmans, 2002).

The most ‘simple’ way to determine partition ratios to particulate material is to separate the water phase and particulates, either by centrifugation and/or filtration (0.45µm is the standard, however sometimes other filter sizes are used),

and measure the concentration of the compound in both the water phase and in the particles. This method is however only reliable if partitioning to dissolved organic matter (DOM) is negligible, otherwise it will underestimate the partition ratio (Lee et al., 2003). Furthermore the method depends on the strength of the solvent used for extraction. In cases where some of the compound is trapped inside particles, full extraction by strong solvents will give information about the actual distribution of HOCs in the sample, however not on the partition ratio (as some of the measured compound is not in equilibrium).

Multiple different methods have been developed in order to separate the compounds sorbed to DOM from the freely dissolved compound. In the complexation-flocculation method separation of the complex-bound compound from the freely dissolved compound is obtained by flocculation (Laor and Rebhun, 1997), whereas in the reverse phase separation method the freely dissolved form is adsorbed on a C_{18}-column assuming that the DOM-bound compound passes the column (Landrum et al., 1984). However, for both methods insufficient separation can lead to bias on partition ratios.

Other techniques which are more appropriate for measuring partition ratios include the method developed during this PhD called passive dosing (**Paper II**), the solid phase micro extraction method (SPME) (Arthur and Pawliszyn, 1990) and the solid phase dosing and sampling method (Ter Laak et al., 2005). These methods do not include phase separation of the sample. Fluorescence quenching (Gauthier et al., 1986) is another method for measuring partition ratios without the need for phase separation. However, fluorescence quenching has the draw-back, that it is restricted to compounds with low hydrophobicity (e.g. four ring PAHs or smaller) because the fluorescence of the freely dissolved concentration has to be measureable (Raber et al., 1998). Furthermore, the assumption that partitioning to all types of organic matter results in static quenching of the fluorescence is questionable (e.g. Puchalski et al. (1992)).

Both the passive dosing method and the solid phase dosing and sampling method employ analytes dosed to the sample and not the native analytes in the sample. The advantage of this is that the partition ratio will then be measureable even in situations where the native analytes are below detection. The advantage of SPME is that the concentration of the native analyte is determined at the same time as the speciation and this additional information can show the relevant

concentrations on each form. However, the passive dosing method avoids some of the analytical problems which can be encountered when using SPME or solid phase dosing and sampling, the most crucial being avoiding a complete mass balance assumption (in passive dosing, analytes sorbed to the glass vial will be replenished by the dosing from the PDMS), but also avoiding fouling problems and ensuring equilibrium in a practical time period (**Paper II**). Furthermore, passive dosing has been shown to be simple, precise and robust.

4.3 Partitioning of PAHs

Most of the literature investigations of the partitioning of PAHs to particulate matter have been conducted using lake, river and saline sediments, although some investigations of partitioning to soil, river and estuarine suspended solids (SS), stormwater particles and different types of soot and biofilms have also been reported (see Table 4).

Partitioning of PAHs to dissolved matter has been investigated in sediment and soil samples. Table 4 shows a selection of partition ratios for fluoranthene found in the literature. The reported partition ratios cover three orders of magnitude. Similar sized ranges can be found for other PAHs (Hawthorne et al., 2006; Kumata et al., 2000). This level of variation cannot be explained by uncertainty in the partition measurements. It is therefore evident that the nature of the particulate matter has a high influence on the partitioning. Studies have shown that the amount and degree of aromaticity of the organic matter influences partition ratios (Gauthier et al., 1987; Neale et al., 2011) and high partition ratios were found to soot particles (Jonker and Koelmans, 2002; Zhou et al., 1999).

Partition in stormwater runoff has not been studied much. Kumata et al. (2000) measured partition in runoff from a highly trafficked road in Tokyo, and in **Paper III** passive dosing measurements of partition in runoff from an industrial and residential area (Albertslund) is reported. Furthermore, partition ratios have been measured in samples from a stormwater pond in Lyon (not published but shown in Figure 7 and Figure 8).

In the passive dosing method, partition ratios can be found by plotting the enhanced capacity of the sample for the substance caused by TSS, E_{TSS}, (this property is explained and defined in **Paper III**) against TSS or particulate organic matter, POM (POM can be used if it is assumed to dominate the sorption

compared to the TSS). The very high correlation between the POM and E_{TSS} in the samples from Albertslund, indicate that the POM is mainly responsible for partitioning (**Paper III**). At this site POM comprises the main fraction of the particulate matter (24-100%, see Figure 9). Stormwater from the pond in Lyon showed much lower organic matter content (2-7%). However, the same overall sorption to TSS was seen in the samples from Lyon compared to the samples from Albertslund (Figure 8).

Table 4: A selection of partition ratios for fluoranthene found in literature. Extended version of table 3 in Paper III.

	Log K (L/kg)	Study	Dosed PAH [3]	Phase separation
Suspended solids & dissolved matter[1]				
Stormwater SS	4.58	**Paper III**	Yes	No[4]
Stormwater POM	5.18	**Paper III**	Yes	No[4]
Traffic soot	6.96	(Jonker and Koelmans, 2002)	No	No[5]
	6.39	(Jonker and Koelmans, 2002)	Yes	No[5]
Wastewater SS	4.3	**Paper II**	Yes	No[4]
Estuary SS	3.8-5.5	(Zhou et al., 1999)	No	Yes
Soil DOM	4.14, 4.18	(Raber et al., 1998)	Yes	No[7]
Organic carbon[2]				
Estuary suspended OC	6.51	(Fernandes et al., 1997)	No	Yes
	4.6	(Tremblay et al., 2005)	Yes	Yes
	5.6-7.2	(Zhou et al., 1999)	No	Yes
Highway runoff OC	4.8-7.2	(Kumata et al., 2000)	No	Yes
Sediment OC	4.32-7.5	(Hawthorne et al., 2006)	No	Yes
	5.4	(Luers and tenHulscher, 1996)	Yes	No[6]
	6.08-6.66	(McGroddy and Farrington, 1995)	No	Yes
	4.75	(Persson et al., 2005)	No	Yes
	4.89;5.32	(de Maagd et al., 1998)	Yes	Yes
Soil OC	4.65-4.82	(He et al., 1995)	Yes	Yes
Biofilm OC	4.5	(Wicke et al., 2007)	Yes	Yes
Sediment DOC	5.18	(Luers and tenHulscher, 1996)	Yes	No[6]
	4.75; 5.41	(Haftka et al., 2010)	No	No[8]
	4.2-5.0	(Brannon et al., 1995)	Yes	Yes
AHA	5.26	**Paper II**	Yes	No[4]

[1]Partition ratios found on a total weight basis. [2]Partition ratios found on an organic carbon basis. [3]Partition ratio calculated based on dosed PAH, [4]measured by passive dosing, [5]measured by poluoxymethylene-SPE partitioning method, [6]measured by gas purge, [7]measured by fluorescence quenching, [8]measured by SPME. SS=suspended solids, POM=particulate organic matter, DOM=dissolved organic matter, OC=organic carbon, AHA=Aldrich humic acid.

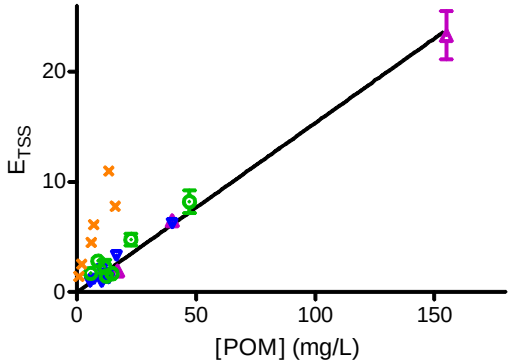

Figure 7: Enhanced capacity caused by suspended solids, E_{TSS}, plotted against the concentration of particulate organic matter (POM). Stormwater samples from Albertslund (green, red and blue symbols) and Lyon (orange crosses). Revised from Figure 4 in **Paper III**.

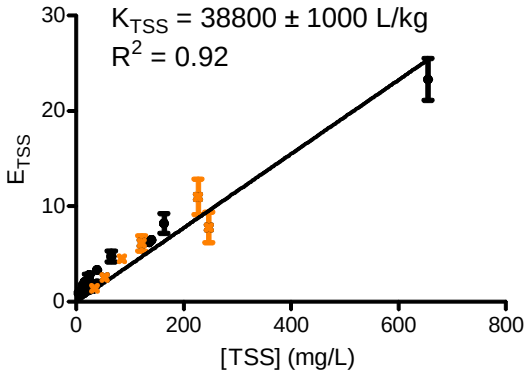

Figure 8: Enhanced capacity caused by suspended solids, E_{TSS}, plotted against the concentration of TSS. Stormwater samples from Albetslund (black dots) and Lyon (orange crosses). Regression is performed on all samples, and the partition ratio and 95 % confidence interval on the partition ratio is given. Error bars show standard deviation on each sample (n=3).

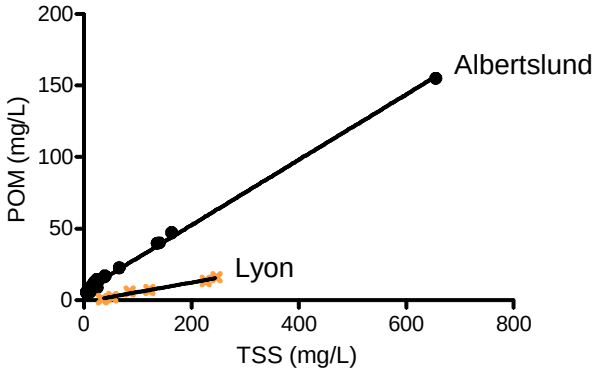

Figure 9: Relationship between particulate organic matter, POM, and total suspended solids, TSS, in samples from the inlet and outlet of a retention pond in Albertslund (black dots) and Lyon (orange crosses).

This can be explained if the particulate organic matter is either very different from the organic matter in samples from Albertslund or if the sorption to inorganic matter play an important role in the sorption of fluoranthene to TSS in stormwater with low POM concentrations.

Whereas Kumata et al. (2000) found highly varying partition in stormwater samples from the same site, this was not the case in our investigations of data from Albertslund and Lyon (Figure 7 and Figure 8). This is probably due to the different measurement method used for the two studies. Kumata et al. (2000) separated the two phases and extracted the PAHs from the particles by dichloromethane. If some of the PAHs on the traffic particulates are not available for partitioning, they will be included in the partition ratio thus obtained. However, the passive dosing method, which was used in **Paper III**, measures equilibrium partitioning. These findings could indicate that whereas the equilibrium partitioning might be relatively constant for the same site over time, the amount of PAHs which are strongly bound can vary. However the varying partition found by Kumata et al. (2000) could also be explained if the type of organic material in the stormwater varied over time at the site they investigated.

As shortly suggested in **Paper III**, the partition ratio measured for fluoranthene by passive dosing can be used to estimate partition ratios for the other PAHs at the same site. The assumption that log K_{ow} and log K_{POM} are linearly related with a slope of approximately one (Witt et al., 2010), leads to the relationship:

$$\text{Log } K_{POM,X} = \log K_{ow,X} - \log K_{ow,fluoranthene} + \log K_{POM,fluoranthene}$$

Solving equation (4), (10) and (11) from **Paper III** for the free fraction, *ff*, leads to the relationship:

$$ff = \frac{1}{K_{POM} \cdot [POM] + K_{DOC} \cdot [DOC] + 1}$$

The estimated free fractions of five other PAHs in the stormwater samples from Albertslund containing the highest and lowest amount of POM, are shown in Table 5. The estimated *ff*s illustrate the large difference in environmental behavior of the PAHs, where naphthalene is mainly freely dissolved in stormwater at this site whereas the 5 and 6 ring PAHs (bottom three in Table 5)

are mainly sorbed to organic matter in the stormwater. The *ff*s also indicates the fraction of the pollutants which are available for uptake in organisms.

Based on the present data, it is suggested for modeling purposes to use a log K_{TSS} of 4.59 for partitioning of fluoranthene to TSS in stormwater if no measurements are done locally.

Table 5: Free fraction of PAHs estimated for the stormwater runoff sample from Albertslund with highest and lowest concentration of particulate organic matter, POM, (The samples can be seen on **Figure 7** as the dots furthest to the right and left, respectively).

	***ff* at max POM**	***ff* at min POM**
Napthalene	0.8	1
Anthracene	0.1	0.8
Fluoranthene	0.04	0.5
Benzo(k)fluoranthene	0.006	0.1
Benzo(a)pyrene	0.005	0.1
Benzo(ghi)perylene	0.004	0.1

5 Sampling priority pollutants in stormwater

In this PhD study focus has been on sampling for chemical analysis. In the following section uncertainties, advantages and disadvantages of the traditional sampling methods are discussed and in Section 5.2, passive samplers are presented and discussed.

5.1 Traditional methods

The three most common stormwater sampling methods are grab, time- and volume proportional sampling. Flow proportional sampling is not as common (sampling a water volume proportional to the flow at constant time intervals as opposed to the volume proportional sampling where a fixed water volume is sampled at variable time intervals proportional to the flow). Special techniques for sampling runoff water close to the source, e.g. roof runoff from down-pipes and road runoff at road level and small ditches, is presented in Skarzynska et al. (2007). In Table 6 advantages and disadvantages for the most common methods are listed.

Table 6: Advantages and disadvantages of grab, time and volume proportional sampling.

	Advantages	**Disadvantages**
Grab sampling	Low cost Special handling can be incorporated No volume restrictions	Represents only one point in time Logistic difficulties (sampling during holidays and at night etc.)
Time proportional sampling	No need to be at site during rain More representative than grab sampling	Rainfall forecast important (start and duration) Two field trips necessary (start of equipment and retrieval of samples) Bias on load estimates at varying flows Heavy equipment/permanent installation
Volume proportional sampling	No need to be at site during rain More representative than time proportional for varying flows	Rainfall forecast important (start, duration and amount) Two field trips necessary (start of equipment and retrieval of samples) Heavy equipment/permanent installation

Time and volume proportional samples are taken either as samples drawn at a single point in time, or as one or more composite samples consisting of a number of sub-samples. It should be noted that representativeness of the time and volume proportional sampling methods depends on the temporal resolution between samples or sub-samples. Therefore when reporting sampling programs it is important to describe the time/volume between sub-samples as well as how many sub-samples are used for composite samples. Detailed description of the sampling is also important because there is not agreement in the scientific community on the terminology used e.g. volume proportional sampling (Ort et al., 2006) is also called flow weighted sampling (Maestre and Pitt, 2005; US EPA, 1992), flow proportional sampling (Lindblom et al., 2011), equal discharge sampling (Ma et al., 2009) and volume paced composite/micro sampling (Ackerman et al., 2011). In order to avoid misunderstandings it should therefore be evident in the description how the sampling was done.

Fletcher and Deletic (2007) found that a monitoring program based on single grab samples taken 1 hour after the rain start resulted in good estimates on annual loadings (even though EMC estimates were not always accurate). However, if the EMC should be accurately described, it has been shown that more than 30 samples has to be taken to estimate EMCs within 20% average error (Ma et al., 2009). It has also been shown that volume proportional sampling is more accurate than time proportional sampling (Leecaster et al., 2002; Ma et al., 2009) and that rainfall depth proportional sampling had accuracies between the two other methods (Ma et al., 2009). Ackerman et al. (2011) conclude that pollutograph sampling (by Ackerman et al. used to denote that a series of samples are taken during the rain event and a sub-set of the samples are analyzed based on the flow data retrieved) has the highest accuracy (how close the measured value is to the true value) and precision (deviation of repeated measurements) for estimating EMCs. However, an adaptive targeted sampling, where the pacing is adjusted based on the anticipated size of rain events can have equally high performance as nearly 100% of the samplings would have EMCs within 10% of the true EMC if the actual rain event size is between 50-100% of the anticipated event size (Ackerman et al., 2011). Sampling campaigns should therefore be designed taking into account the needed accuracy and precision of the results.

The uncertainties in estimating EMCs when using automated samplers originate from variations in space as well as in time. Vertical distribution of suspended solids (and associated pollutants) can be observed in flow channels with larger particles being transported near the bottom, and for rivers the horizontal distribution can be important as well (Horowitz, 2008). Roseen et al. (2011) found that sediment EMCs were well represented using an automated sampler compared to measurements where they collected the total runoff volume of the event for analysis. However larger particles may fall out of suspension in the sampling hose if the suction velocity is lower than the flow velocity at the site. Suggestions on how to optimize the intake for autosamplers have been published by Gettel et al. (2011) who designed a multiple tube intake fitted with a wing to provide lift.

5.2 Passive sampling

There exist two types of passive samplers. Diffusion based passive samplers and flow-through passive samplers. Most of the literature published so far, and most of the passive samplers developed are diffusion based. The following section describes these passive samplers, and is based on work published in (Pettersson et al., 2010). However, when monitoring stormwater discharges over periods of weeks or months to evaluate average concentrations or loads, time-dependent sampling (as obtained by diffusion based passive samplers) is not suitable because the dry periods between rain events would be included in the measurements. This would bias the measurements of the discharged concentrations. In this PhD project, it was therefore decided to test a flow-through passive sampler, SorbiCell, which can be installed so that sampling depends on the water velocity at the site. This passive sampler type is described further in section 5.2.2, however, an important difference between the two types of samplers is that diffusion based samplers by nature only samples the freely dissolved and labile species, whereas flow-through samplers can collect any fraction which is able to pass through the inlet filter.

5.2.1 Diffusion based passive samplers

The principle behind diffusion based passive sampling is that a receiving phase, which has a high affinity for the compounds of interest, is placed in the medium to be sampled; e.g. water. The sampler can be with or without a membrane separating the receiving phase and the sampled phase. The passive sampler can then, based on chemical or physical properties of the membrane, receiving phase

and analytes, selectively accumulate chemical substances by diffusion from the water to the sampler. During the last decades, a lot of work has been put into the development of these passive samplers, and a range of reviews have been published covering the area (Namiesnik et al., 2005; Seethapathy et al., 2008; Stuer-Lauridsen, 2005; Vrana et al., 2005). Also, comparative studies including many different passive samplers are now being reported (Allan et al., 2009; Allan et al., 2010).

In Table 7 advantages and disadvantages of diffusion based passive sampling are listed. The main advantage is the time-integrative measurements obtained. There are both positive and negative practical aspects of passive sampling (which aspects are most important will depend on the sampling campaign considered), and the fact that diffusion based passive samplers only sample the freely dissolved and labile species can be either an advantage or disadvantage depending on the aim of the study.

Table 7: Advantages and disadvantages of diffusion based passive sampling.

	Advantages	**Disadvantages**
Passive sampling	Continuous sampling Low detection limits can be obtained through high pre-concentration at site Reduced need for clean-up of the extract Freely dissolved and labile species are sampled simulating the species available for uptake in biota. Transport of large water volumes are not necessary	Risk of contamination for some of the samplers which are effective air samplers as well. Freely dissolved and labile species are sampled, however total concentrations are regulated Vandalism/loss of samplers Fouling

There are two different uptake mechanisms in diffusion based passive samplers: absorption and adsorption (see Table 8). Passive samplers targeting HOCs generally work by absorption (partition based samplers) and passive samplers targeting polar organic compounds and heavy metals work by adsorption (surface bonding).

Table 8: Overview of the most common passive samplers.

Analytes	**Hydrophobic organic compounds**		**Polar organic compounds**	**Metals**
Accumulation mechanism	Absorption		Adsorption	
Uptake regime	Kinetic	Equilibrium	Kinetic	
Samplers	SPMD LDPE Silicone rubber Chemcatcher	SPME Stir bar sorptive extraction	Chemcatcher POCIS	Chemcatcher DGT
Calibration	Sampling rate R_s can be found by PRCs for each deployment	Partition ratio K_{sw} found by lab calibration or from log K_{ow} relations	Sampling rate, R_s, are estimated in lab/field calibrations. They vary depending on the analyte, velocity around the sampler, temperature and biofouling.	

Uptake in partition based passive samplers can be described by the partitioning theory:

$$C_s = C_w K_{SW}\left[1-\exp\left(-\frac{R_s t}{K_{SW} V_s}\right)\right]$$

where C_s is the concentration in the sampler, C_w is the concentration in the water, K_{sw} is the partition ratio between the sampler and the water, V_s is the volume of the sampler, R_s is the sampling rate and t is the sampling time (Huckins et al., 1993). Depending on the configuration of the sampler and the deployment time, partition based passive samplers can operate as either kinetic or equilibrium samplers (see Figure 10).

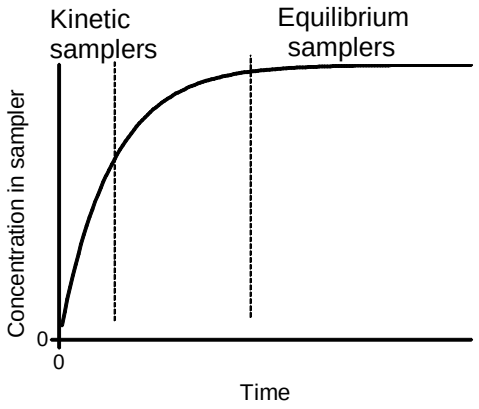

Figure 10: Uptake in kinetic and equilibrium partitioning passive samplers (Allan et al., 2006b).

Equilibrium passive samplers are deployed for a period sufficient to obtain near-equilibrium between the sampler and water. Requirements for equilibrium sampling are that the response time of the sampler should be shorter than fluctuations in analyte concentration at the site and that the amount of the analyte taken up by the sampler should be much smaller than the amount of the analyte in the sampled water in order to avoid depletion of the sampled water. This method is equivalent to grab sampling, but it has the advantages that transportation of large sample volumes is avoided, cleaning of extracts can be minimized and lower detection limits often are obtained as the extraction is performed *in situ*. An example of this is the stir bar sorptive extraction technique (Baltussen et al., 1999). The same principle is also used in laboratory extraction procedures such as solid phase microextraction (SPME) (Arthur and Pawliszyn, 1990).

Kinetic passive samplers operate in the kinetic uptake regime during the whole deployment. The uptake at each point in time is dependent on the (varying) concentration at the site. Therefore this type of sampler operates as a time-integrative sampler. Many different designs of kinetic passive samplers have been described in the literature (see Figure 11 for examples). Kinetic samplers, which have been used quantitatively in the field and which are commercially available, include (Table 8): semi permeable membrane devices (SPMDs) (Huckins et al., 1990) used for hydrophobic substances, polar organic chemical integrative samplers (POCISs) (Alvarez et al., 2004) used for polar organic substances, diffuse gradient in thin films (DGTs) (Davison and Zhang, 1994; Zhang and Davison, 1995) used to sample metals and Chemcatcher (Kingston et al., 2000) which have different versions for sampling of hydrophobic and polar organic substances as well as metals.

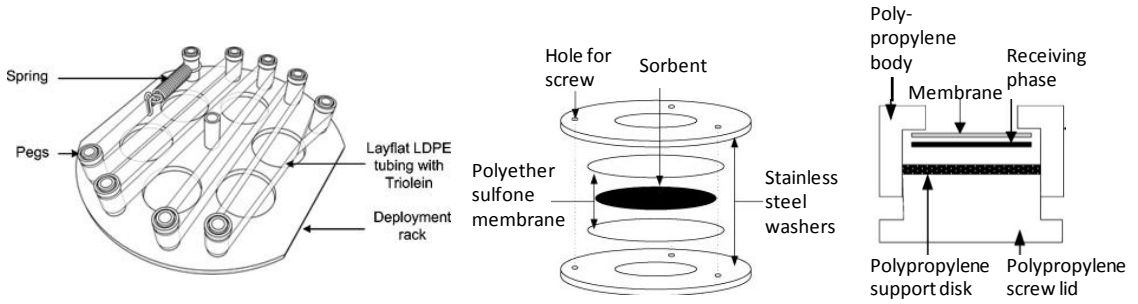

Figure 11: SPMD (left), POCIS (middle) and Chemcatcher (right). Reprinted from Seethapathy et al. (Seethapathy et al., 2008) with permission from Elsevier.

Silicone rubber and low density polyethylene (LDPE) rods or strips (Booij et al., 2002; Müller et al., 2001) are also used widely (Allan et al., 2009; Allan et al., 2010; Mills et al., 2011). They are not possible to purchase as a passive sampler product, but the materials are easy to prepare.

When calculating (average) concentrations from the sampler measurements, the partition ratio between the analyte and the sorbent in the sampler should be known for equilibrium samplers, and the sampling rate should be known for kinetic samplers (Table 8). Partition ratios can be estimated based on empirical relationships with log K_{ow} (Greenwood et al., 2007; Huckins et al., 2006).

The sampling rate, R_s, depends on factors such as sampler configuration, temperature, biofouling and velocity around the sampler as well as on the specific analyte. In order to find the appropriate sampling rate for each specific deployment, performance reference compounds (PRCs) are used in absorption based passive samplers. PRCs are compounds which do not occur in the environment, but are added to the sampler before deployment. The elimination rate of the PRC from the sampler is then used to compensate for the influence of the environmental factors at each deployment. The compound specific effect on the sampling rate can be estimated based on relationships with log K_{ow} (see e.g. Huckins et al. (2006) and Vrana et al. (2007)), and the sampling rate varies linearly with the surface area of the sampler (Alvarez et al., 2004; Huckins et al., 2006; Zhang et al., 2008).

Unlike the absorption based passive samplers, no theoretical models based on chemical properties are available for predicting the uptake of analytes into adsorption based passive samplers (Mills et al., 2011). For passive samplers based on adsorption, sampling rates for each analyte and set of environmental conditions therefore has to be found from calibration experiments. Efforts are being made to get around this problem by designing the passive sampler so that the membrane is rate limiting for the uptake and elimination of analytes (Mazzella et al., 2007; Persson et al., 2001; Tran et al., 2007).

5.2.2 Flow-through passive samplers

The flow-through passive sampler, SorbiCell, consists of a cartridge filled with a sorbent and a tracer salt (Figure 12) (de Jonge and Rothenberg, 2005).

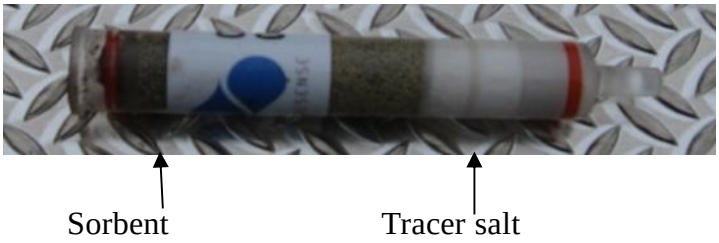

Figure 12: The flow-through passive sampler, SorbiCell.

The uptake mechanism of the flow-through sampler is different from the other passive samplers described above, because uptake of the analytes is not based on diffusion of the analyte towards the passive sampler, but rather on uptake from water passing through the sampler. The original method used to induce water flow through the sampler was by mounting the sampler on a submerged reservoir with atmospheric pressure inside (Rozemeijer et al., 2010). The pressure gradient from the water column above the sampler resulted in a slow flow of water through the sampler.

During this PhD project another installation method was tested (**Paper IV**). This method consists of placing the sampler directly in the water letting the momentum from the water velocity induce the flow through the sampler. This installation method results in a varying sampling rate depending on the velocity. The sample would ideally represent the load of the analyte passing the sampling point. However the necessary assumptions in order to obtain this is that (a) the water velocity is linearly proportional to the water flow at the site, (b) there is no uptake in the sampler when there is no flow in the system, (c) the water velocity at the site is proportional to water flow through the sampler and not changing over time and (d) the water composition of the water passing the sampler can represent the composition of the water throughout the cross-section of the channel/ditch (spatial representativeness).

In **Paper IV** the first three assumptions are discussed. It is argued that (a) even though the relationship between the water velocity and flow changes over time, this is not crucial for the sampling method, (b) the maximum uptake of analytes in the sampler during dry weather is < 50% of the uptake during rain, and most likely much less, (c) proportionality between the velocity at the site and flow through the sampler is reasonable but not exactly good (Kronvang et al., 2010).

The last assumption (d) is relevant for all sampling methods and has been discussed above (Section 5.1). Furthermore, based on literature findings in **Paper IV** it is concluded that sampling of the particulate fraction smaller than e.g. 150 µm would comprise the majority of the pollutants in the stormwater. However the actual pore size of the spheriglass inlet filter used in the sampler is not known.

Flow-through passive samplers targeting heavy metals and samplers targeting PAHs were tested during this PhD project. Results from the PAH measurements (Table 9) show that the passive sampler has high detection limits (LODs) for the PAHs resulting in detection of very few PAHs. For some of the PAHs detection limits were higher than the AA-EQSs. Phenanthrene was the only PAH detected in both the replicates during the first installation period, however the precision was poor with replicate concentrations of 0.93 and 0.05 µg/L.

Table 9. Dublicate (period 1) and triplicate (period 2) PAH concentrations measured by flow-through passive samplers.

	AA-EQS	Period 1		Period 2		
mL sampled		90	220	320	310	370
Naphthalene	2.4	<0.29	<0.12	<0.08	<0.08	<0.07
Acenaphthylene		<0.06	<0.02	**0.06**	<0.03	<0.03
Acenaphthene		<0.06	<0.02	<0.02	<0.02	<0.01
Fluorene		<0.29	<0.12	**0.03**	<0.02	<0.01
Phenanthrene		**0.93**	**0.05**	<0.16	<0.16	<0.14
Anthracene	0.1	<0.06	<0.02	<0.16	<0.16	<0.14
Fluoranthene	0.1	<0.12	<0.05	<0.08	<0.08	<0.07
Pyrene		<0.12	<0.05	<0.03	<0.03	<0.03
Benzo(a)anthracene		<0.12	<0.05	**0.06**	<0.02	<0.01
Chrysene		<0.12	<0.05	<0.02	<0.02	<0.01
Benzo(b)fluoranthene	}0.03[1]	<0.12	<0.05	**0.04**	<0.03	<0.03
Benzo(k)fluoranthene		<0.06	<0.02	<0.03	<0.03	<0.03
Benzo(a)pyrene	0.05	<0.06	<0.02	**0.1**	<0.03	<0.03
Benzo(ghi)perylene	}0.002[2]	<0.12	<0.05	**0.13**	<0.03	<0.03
Indeno(1,2,3-cd)pyrene		<0.12	<0.05	<0.03	<0.03	<0.03
Dibenzo(ah)anthracene		<0.12	<0.05	<0.03	<0.03	<0.03
sum 16 PAH EPA		<6.99	<2.76	<1.9	<1.92	<1.64

[1]Sum of Benzo(b)fluoranthene and Benzo(k)fluoranthene, [2]Sum of Indeno(1,2,3-cd)pyrene and Benzo(ghi)perylene.

For the second installation period Benzo(a)anthracene, Benzo(a)pyrene, Benzo(ghi)perylene, acenaphthalene, fluorene, Benzo(b)fluoranthene were detected, but only in one of the 3 replicates.

It was also seen (Table 9 top) that there was a large variation in the amount of water passing through the samplers in period 1, whereas during period 2 the sampled amounts of water were not as varying as for period 1. Re-sizing the flow-through passive sampler for PAHs in order to allow larger volumes of water to pass through the sampler, is essential to obtain the necessary low detection limits.

The results of the heavy metal passive samplers, presented in **Paper IV,** showed comparative concentrations in the inlet to the retention pond in Albertslund measured by passive sampling, by volume proportional sampling and using a dynamic stormwater quality model. This indicates that the assumptions and approximations are reasonable in order to get an estimation of the average concentrations at the site. However more research is needed in order to evaluate the accuracy and precision of this type of sampling and to quantify the uncertainty caused by these assumptions on the uptake of analytes in the flow-through passive sampler when installed velocity dependant.

6 Monitoring of priority pollutants in stormwater runoff using passive samplers and models

The WFD requirements for monitoring are simple and, as discussed in section 2.1 and illustrated in Figure 4 (p. 8), based on a minimum number of grab samples from surface waters. There are possibilities for using many other sampling techniques (see Table 1) when designing surface water monitoring strategies (see also Allan et al. (2006a)). In Figure 13, the role of time and velocity dependant passive samplers, the passive dosing method and modeling in WFD monitoring is illustrated.

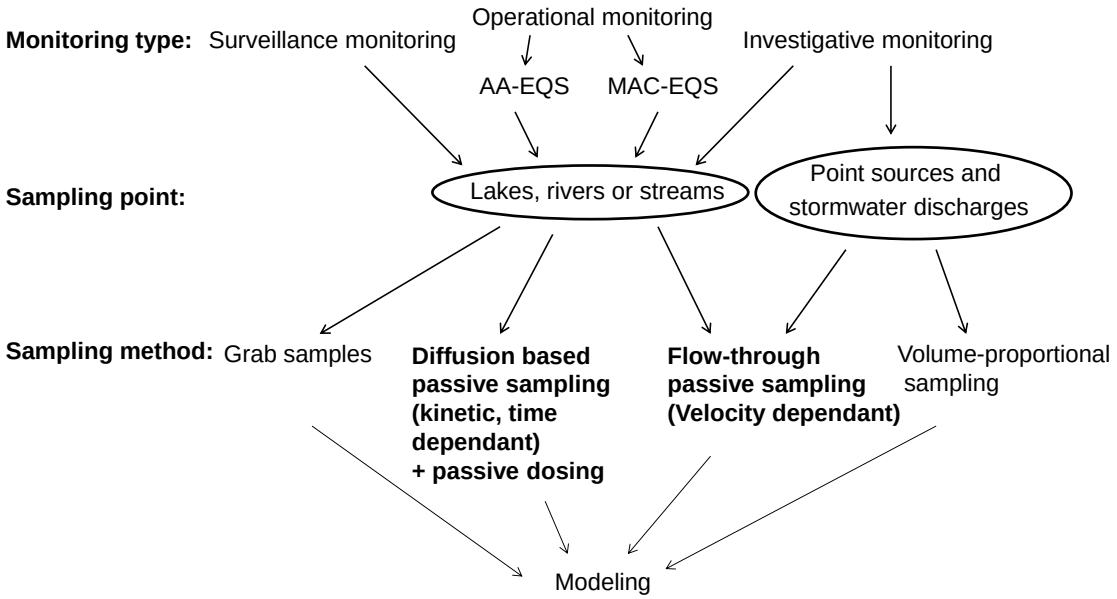

Figure 13: Possibilities for alternative surface water monitoring strategies.

The most obvious aim where (kinetic) passive samplers can be used as an alternative sampling method is for surveillance and operational monitoring (targeting AA-EQS) of surface waters with slow or medium concentration dynamics. Monthly passive sampler installations would, by integrating the water concentrations over time, yield more reliable information than monthly grab samples. Lower detection limits are also often obtained with passive samplers than with water samples, improving the possibility that detection limits in the range of the EQSs can be reached. Since the EQSs are defined for total

concentrations, a conversion of the dissolved concentrations measured by the diffusion based passive samplers is needed. The passive dosing method developed during this PhD can be used for this purpose. This can practically be done by measuring partitioning in samples taken when the passive samplers are installed and collected.

The flow-through passive sampler can also be a useful alternative to grab sampling for surveillance or operational monitoring (targeting AA-EQS) in flowing surface waters (rivers or streams). Depending on whether the aim of the sampling is to estimate loads or average concentrations in the surface waters, time or velocity dependant installations can be chosen. The flow-through passive sampler can also be dimensioned for low detection limits as required for comparison with the EQSs.

None of the traditional methods (grab, time or volume proportional sampling) are suitable for finding the maximum concentrations in surface waters, and passive samplers are not suitable either, as they have an integrative nature. Sensors or biological early warning systems are therefore more appropriate if maximum concentrations should be evaluated (however, sensors are still very expensive).

For investigative monitoring, the flow-through passive sampler can also be a useful tool. Loads from the sources to the receiving waters can be evaluated using flow-through passive samplers installed velocity dependently. For a water body where multiple stormwater discharges contribute to the loads of PPs, passive sampling is suggested as a cost-efficient alternative to volume proportional sampling e.g. in order to evaluate the role of each catchment on the amount of PPs discharged to the water body and to find the best treatment strategy for the stormwater discharges.

Evaluation of pollutant loads or concentrations in stormwater runoff based on water quality measurements at a particular site is always based on some kind of hypothesis or model of the system. The simplest model is to assume that (sometimes few) measured concentrations represent the general state of the system. For example, discharge permits can be based on a low number of grab samples from a site (e.g. 4 per year (Copenhagen Municipality, 2008) or 12 per year (European Commission, 2000)). If ‘compliance’ or ‘non-compliance’ is evaluated based on these measurements, representativeness of the samples is

assumed even though the permit does not explicitly state this and the supervising authority may be well aware that this is a coarse simplification. However all models are simplifications of the system, and it is important to choose the model according to the aims of the investigation.

Whereas the use of models for design purposes are relatively common, use of models for permit compliance purposes are rarely seen. An example of this has been published by Bachhuber (2010), who reported that a modeled annual average concentration of TSS was accepted by the regulatory authority for compliance with the discharge permit of an industrial area in Wisconsin. However, the combination of modeling and sampling for monitoring purposes has the strong advantage that uncertainty can be lowered as seen in **Paper V**. Furthermore, the use of the model can expand the monitoring period beyond the actually sampled period by evaluating the AA concentration based on longer rain series and thereby improve the determination of the proper level of treatment for stormwater discharges.

6.1 Modeling stormwater quality

A range of stormwater runoff quality models have been developed over the years (Elliott and Trowsdale, 2007; Obropta and Kardos, 2007; Tsihrintzis and Hamid, 1997). Some models are simple and some are complex, some models are deterministic, either conceptual (trying to describe the processes governing release and transport of pollutants) or regression based (using catchment and/or rainfall characteristics as parameters), and others are stochastic. The time scale adopted by the models also differs, where some models targets annual loads, others are event based, and some are dynamic models with time steps from minutes to hours.

Examples of regression models can be found in Kayhanian et al. (2007) for highway runoff constituents and the American national stormwater quality database (NSQD) and the nationwide urban runoff program (NURP) studies for mixed stormwater runoff (Maestre and Pitt, 2005; US EPA, 1983). For heavy metals it has been found that lognormal distributions adequately represent both the storm to storm variations in pollutant EMCs at an urban site, and the site-to-site variations in median EMCs (US EPA, 1983). However, since such regression models require large amounts of data for calibration (Mourad et al., 2005),

regression models for the less commonly monitored organic pollutants have not yet been published.

While regression models are based on data only, conceptual models are formulated based on knowledge of the system and then calibrated with measurements in the system. Many conceptual deterministic models have been described (SWMM, STORM, MOUSE, MUSIC, etc. (Elliott and Trowsdale, 2007; Obropta and Kardos, 2007)). Most of these models are developed for particulate matter, simulating the buildup and wash-off of particulate matter from surfaces. These models can be used for pollutants which are sorbed to and transported by particulate matter and have the same pattern/mechanism of release from sources in the catchment as the particulate matter. A conceptual accumulation wash-off model was e.g. calibrated by Lindblom et al. (2011) for heavy metals. The same model was incorporated in an integrated model for stormwater systems (Vezzaro et al., 2012). Only few have calibrated conceptual stormwater quality models for organic pollutants (in Vezzaro et al. (2011) and **Paper V** a stormwater quality model was calibrated for fluoranthene), and application of a stormwater quality model for phthalates and nonylphenols based on source estimations for input but without calibration showed poor performance (r^2 was 0.01 and 0.03) (Bjorklund et al., 2011).

There are different sources of uncertainty in any model: model structure uncertainty, parameter uncertainty, uncertainty from the quality and quantity of calibration data, and input data uncertainty (Butts et al., 2004; Haydon and Deletic, 2009). Model structure uncertainty is often not evaluated for stormwater quality models (even though comparisons of models in relation to model performance have been reported (Dotto et al., 2011)), but model structure uncertainty have been investigated for hydrological modeling (Butts et al., 2004). Model parameter uncertainty can be investigated through parameter sensitivity analysis (Dotto et al., 2011; Vezzaro and Mikkelsen, 2012), input data uncertainty has e.g. been investigated by Haydon and Deletic (2009) for a coupled pathogen indicator-hydrologic catchment model, and the influence of the quantity of data used for calibration have been investigated by e.g. Mourad et al. (2005). Furthermore, the choice of calibration method can have an effect on uncertainty estimation (Dotto et al., 2012).

Model uncertainty estimation can be done using different methods. Kanso et al. (2005) showed how a method based on Bayesian theory can be used to estimate parameter uncertainty in urban runoff quality models. This method consists of assigning a probability distribution to the model parameters and then updating the distributions based on the new data collected. Another method used to estimate model uncertainty is the General Likelihood Uncertainty Estimation (GLUE) technique (Beven and Binley, 1992). This method is based on the realization that different parameter sets (called 'behavioral') can obtain the same performance when comparing the model to measurements. The behavioral parameter sets are chosen based on a likelihood measure which can be chosen by the modeler. The model prediction bounds are then found from the behavioral parameter sets. The GLUE method was used for calibration of a dynamic stormwater quality model by Vezzaro et al. (2012) and in **Paper V**.

Depending on the use of the models, there are different requirements for the precision of the models. The more detailed information required from the model, the more detailed data is necessary for calibration. One approach for gathering calibration data is to sample 'mean' or 'representative' rain events (e.g. sampling for the NURP and NSQD monitoring program includes only 'representative' events: "Only samples from rain events greater than 0.1 inches, and close to the annual mean conditions, were considered valid for the analysis" (Maestre and Pitt, 2005)). However, it has been shown that calibration of a stormwater quality regression model on a sub-set of 6 events which included an event with markedly higher concentrations than the other events significantly improved the accuracy of the estimate of loads from a catchment compared to a sub-set of events excluding the high concentration event (Bertrand-Krajewski, 2007). This highlights the importance of including extreme events in calibration of models. If the variability of the system should be represented well enough by the model to evaluate peak concentrations, the data set used for calibration should include even more detailed information such as pollutographs during the extreme events.

6.2 Use of a dynamic stormwater runoff quality model for evaluating monitoring strategies

In this PhD project, a conceptual dynamic stormwater quality model was used (Lindblom et al., 2011; Vezzaro, 2011; Vezzaro and Mikkelsen, 2012). The model consists of a hydrological submodel, where generation and routing of runoff is simulated, and a water quality submodel where accumulation and

release of pollutants is simulated. The runoff model was in Vezzaro et al. (2012) coupled to a stormwater treatment unit model (Vezzaro et al., 2010). However in this PhD project only the runoff module was used (**Paper V**). Calibration of the model using a general likelihood uncertainty estimation (GLUE) method is described in Vezzaro et al. (2012), Vezzaro and Mikkelsen (2012) and **Paper V**.

The aim of the use of the stormwater model was to evaluate the information gained by different sampling strategies at the catchment in Albertslund. Therefore simulation of the different sampling methods was implemented in the model. Volume proportional sampling was simulated by sub-sampling the model at a given increment in the modeled runoff volume. Passive samplers were simulated as flow proportional continuous sampling of the modeled concentration when flow exceeded a given threshold (as described in **Paper V**). In reality the sampling rate is related to the water velocity rather than the flow in the system as discussed in **Paper IV**. However this was not taken into account in the model used here which is based on runoff flow and does not include velocity as a model parameter.

The measurements used for calibration of the model were not chosen to be 'representative' or 'mean' for the catchment. All sampled events were used. However, since electricity was not available at the sampling site the samplers had to be brought home to charge. They were therefore only set up when rain was expected. This could lead to biases arising from the selection of sampled events since flashy showers which were not expected in the weather forecasts were not represented. Very small events were also not represented because the sampled volume was not enough for analyses. Furthermore, the chance of sampling extreme events is very low in a sampling campaign consisting of 10 events sampled over one year. In this respect information gained from passive samplers has the great advantage that all the events occurring during the installation period are incorporated in the measurements. The chance of sampling during extreme events is therefore enhanced. However the robustness of the passive samplers in extreme events has not been tested, so loss of samplers could occur.

In Figure 14 AA concentrations of Cu and Zn are shown estimated by different datasets and models. In scenario (a) and (b) a lognormal distribution is assumed for 6 and 10 events respectively, and the lognormal mean and 50 and 90% confidence limits are shown (corresponding to the 5, 25, 75 and 95 fractiles).

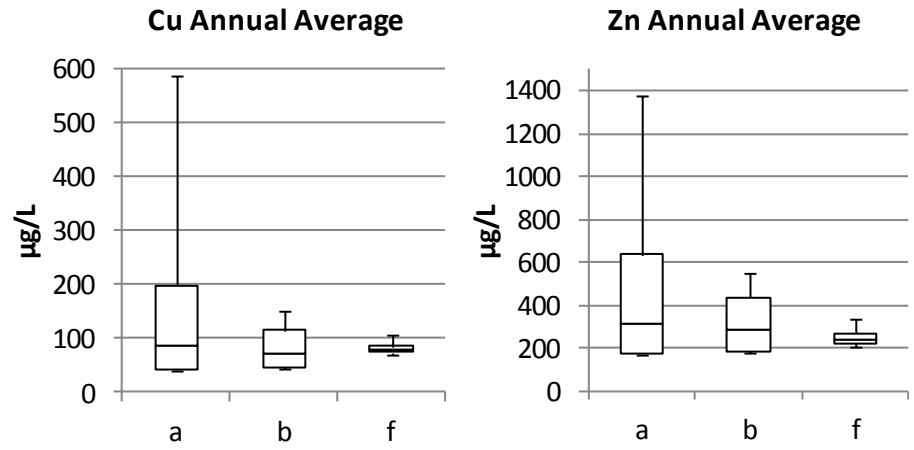

Figure 14: Annual average concentration of Cu (left) and Zn (right) in stormwater runoff in Albertslund. Mean and 5, 25, 75 and 95% fractiles are estimated using (a) a lognormal distribution based on 6 EMCs, (b) a lognormal distribution based on 10 EMCs, (f) a dynamic model based on 6 EMCs and passive sampler measurements. The figure is an extract from Figure 2 in **Paper V**.

In scenario (f) the dynamic stormwater quality model was used and calibrated with 6 EMCs and a passive sampler measurement. The calibration using the GLUE method results in a number 'behavioral' parameters set. These parameter sets are used to evaluate the uncertainty of the model, and in Figure 14 the median, 5, 25, 75 and 95% fractiles of runs using these parameter sets are shown.

It was seen that using a simple stochastic model based on lognormal distribution of EMCs lead to high uncertainty on the annual average (AA) concentration in stormwater estimated from 6 EMCs (scenario a in Figure 14 and in **Paper V**). Narrower confidence bounds were obtained by using more events for the estimation (scenario b in Figure 14). The uncertainty bounds were however narrowed even further by using the dynamic stormwater quality model for estimating the AA concentrations. For fluoranthene, where the annual average was in the range of the current EQSs, the model uncertainty bounds were reduced to around 50%, which is the performance criteria required for methods of analysis at the level of the relevant EQS in the WFD (see **Paper V** and (European Commission, 2009)).

Bertrand-Krajewski (2007) saw that using different data-sets for calibration of a pollutant runoff model led to differences in the estimated annual average

concentrations. This was also to some extent observed at the site investigated in **Paper V**. This indicated that the initial data set did not comprise enough events or appropriate events in order to describe the system fully. The parameters which are calibrated in the quality model are the pollutant accumulation rate, dry weather removal rate and rainfall washoff coefficient (see **Paper V**), and these parameters are influenced by the hydrological parameters such as runoff coefficient and initial loss. It was seen that calibration using a combination of passive sampler measurements and volume proportional samples stabilized the model by determining an appropriate average level (pollutant accumulation and dry weather removal rate) and resulted in smaller uncertainty intervals than calibration based on volume proportional samples only.

The monitoring strategy which resulted in the smallest uncertainty bounds, were the use of 6 EMCs and one passive sampler measurement to calibrate the dynamic stormwater quality model (as seen in scenario (f) in Figure 14 and in **Paper V**). This strategy minimizes the measurement costs since passive sampling is less costly than volume proportional sampling.

7 Conclusions

This PhD thesis provides an overview of important issues for monitoring of PPs in stormwater. The most important PPs identified in stormwater were the heavy metals Cu and Zn, PAHs, DEHP and the pesticides used locally (here glyphosate). These PPs were found in all of the 6 stormwater screening samples from different locations in the Copenhagen area. These PPs also represent the main stormwater relevant pollutant groups and sources found in literature.

Partitioning of pollutants between particulate matter and freely dissolved forms in stormwater is important for the toxicity of PPs, for treatment of PPs, but also for sampling of stormwater because e.g. most passive samplers only sample the dissolved and labile forms. The sorption capacity of stormwater can be characterized using a novel analytical method which was developed during this PhD project for measuring partitioning of hydrophobic organic compounds in aqueous samples. This method proved to be simple to use and provide precise and robust partition measurements. The method revealed a $\log K_{TSS}$ of 4.59 for fluoranthene in stormwater from a catchment in Denmark and another in France. Calculations based on the partitioning measurements of fluoranthene and inherent properties of the other PAHs showed the different partitioning of the PAHs in stormwater, with naphthalene being mainly freely dissolved in stormwater, fluoranthene being mainly sorbed to particulate matter during the first part of the runoff events but up to 50 % freely dissolved during the last part of events, and benzo(a)pyrene being mainly sorbed to particulate matter in stormwater.

Most of the passive samplers described in literature cannot be used reasonably in stormwater systems since time-weighted averages over weeks to months do not yield useful information in systems with long periods of no-flow. However, a flow-through passive sampler, SorbiCell, can be used because it can be installed in a manner where sampling is dependent on the velocity of the water in the system thus facilitating sampling primarily during runoff events. Tests of this sampler in a stormwater drainage tunnel revealed concentrations of heavy metals comparable to total concentrations measured by volume proportional sampling and to flow-weighted concentrations obtained using a dynamic stormwater quality model. The advantage of using this passive sampler is the integrative nature of the sampling, that sampling is not limited by the availability of personnel during odd hours, and that transport of heavy and large equipment and

large sample volumes is avoided. The disadvantages are that the samplers are not validated yet and that the sampling uncertainties and biases have not been fully quantified. Furthermore there are technical challenges such as avoiding blockage by leaves and debris and ensuring a high water velocity at the sampler installation.

Many stormwater quality models exists, however there is no consensus on how much information is needed to evaluate mean concentrations at site level. The advantage of using models for monitoring purposes is that information about the system beyond the time interval of sampling can be obtained based on knowledge of processes and observed patterns. Furthermore, statistics on the annual average concentrations can be obtained from modeling of rain series. Model prediction bounds for annual average concentrations obtained by a dynamic stormwater quality model were narrower than using simple stochastic methods. The use of passive sampler measurements in combination with volume proportional measurements for calibration reduced the model prediction bounds on annual average concentrations more than simply increasing the number of volume proportional samples.

The work done during this PhD project illustrates a framework for monitoring where passive samplers and models are used. It is an important step towards general acceptance and use of passive samplers and models in monitoring programs for stormwater runoff. This can provide practical and economical advantages compared to traditional methods and can enable larger scale monitoring of PPs in stormwater to be feasible.

8 Future research

Due to the very high ambitions outlined by the EU WFD for the water quality of surface waters, including phasing out of emissions of the traffic related PAHs, urban stormwater management is crucial. The limited knowledge on emissions of some of the priority pollutants to surface waters necessitates monitoring campaigns. As many of the EQSs defined are lower than the detection limits of the standard analytical methods used by commercial laboratories, there is a great need for development of analytical methods to detect pollutants in pg/L concentrations.

In this study the flow-through passive sampler, SorbiCell, was tested in stormwater runoff. Even though the test showed promising results for velocity dependant sampling of stormwater runoff, work is still needed in order to understand and describe the sampling method. In order to gain more information about the sampler, lab-scale experiments can be designed to investigate:

- the relationship between the water velocity and the flow through the sampler,
- possible decrease in response over time due to clogging for long-time installations,
- the uptake of analytes by the sampler during stagnant flow-conditions,
- the pore size of the spheriglass filter.

There is also a need for standardized installation methods which avoids problems with blocking of the sampler by leaves etc. and ensures controlled flow conditions. Furthermore, even though many passive samplers have detection limits in the pg/L range (depending on the actual installation), the tested flow-through passive sampler had higher detection limits in this work. Optimization of the passive sampler for lower detection limits is important in order to be able to use it for monitoring of organic pollutants in stormwater runoff. The use of flow-through passive samplers for pesticide monitoring also has great potential, and development of a resin for binding of hydrophilic pesticides such as glyphosate would be useful.

More measurements of the partitioning in stormwater samples would also be very interesting in order to see whether the partition ratios found in this study are in

fact as globally applicable as indicated by the results obtained so far. With the passive dosing method developed here, these measurements are straight forward.

More generally there is a need to accredit the passive samplers and define their role in monitoring. Inter-laboratory analysis tests and installations of different types of passive samplers at the same site are currently being done and enable comparisons between sampler performances. However there is a need for a standard method to evaluate the biases and uncertainties of passive samplers at relevant concentration levels and field conditions similar to the use of reference materials in standard quality control of laboratory analyses.

Further development of stormwater quality models is also needed. Especially the ability of the model to predict extreme events and dynamics throughout the events needs to be investigated further in order to improve the ability of the models to relate to MAC-EQSs. Criteria for uncertainty and calibration of models when used for compliance purposes also need to be defined. Future research should include larger monitoring programs using passive samplers over long periods, volume proportional sampling over short periods, and stormwater quality models to evaluate the statistical features of AA concentrations and maximum concentrations in stormwater discharges.

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10 Papers

I. **Birch, H.**, Mikkelsen, P.S., Jensen, J.K., Lützhøft, H.-C.H. (2011). Micropollutants in stormwater run-off and combined sewer overflow in the Copenhagen area, Denmark, *Water Science and Technology*, **64** (2), 485-493. DOI: 10.2166/wst.2011.687.

II. **Birch, H.**, Gouliarmou, V., Lützhøft, H.-C.H., Mikkelsen, P.S. and Mayer, P. (2010). Passive Dosing to determine the speciation of hydrophobic organic chemicals in aqueous samples, *Analytical Chemistry*, **82** (3), 1142-1146. DOI: 10.1021/ac902378w.

III. **Birch, H.,** Mayer, P., Lützhøft, H-C.H. and Mikkelsen, P.S. (in revision) Partitioning of fluoranthene between free and bound forms in stormwater runoff and urban waste waters using passive dosing, *Water Research.*

IV. **Birch, H.,** Sharma, A.K., Vezzaro, L., Lützhøft, H.-C.H. and Mikkelsen, P.S. (manuscript). Velocity dependant sampling of micropollutants in stormwater using a flow-through passive sampler. *Environmental Science and Technology. 2012*

V. **Birch, H.,** Vezzaro, L. and Mikkelsen, P.S. (accepted) Model based monitoring of stormwater runoff quality. *In proceedings of the 9th international conference on Urban Drainage Modelling, Belgrade, 2012.*

The papers are not included in the www-version, but can be obtained from the Library at DTU Environment.

Department of Environmental Engineering
Technical University of Denmark
Miljoevej, Building 113
DK-2800 Kgs. Lyngby, Denmark
(library@env.dtu.dk)

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DTU Environment
Department of Environmental Engineering
Technical University of Denmark

Miljoevej, building 113
DK-2800 Kgs. Lyngby
Denmark

Phone: +45 4525 1600
Fax: +45 4593 2850
e-mail: reception@env.dtu.dk
www.env.dtu.dk

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